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CXIII.—*The Electro-affinity of Aluminium. Part III.  
The Acidity and Constitution of Aluminic Acid.*

By JAROSLAV HEYROVSKÝ.

The investigations of Slade (*Zeitsch. Elektrochem.*, 1911, **17**, 261), Blum (*J. Amer. Chem. Soc.*, 1913, **35**, 1499; 1914, **36**, 2383), and Hildebrand (*ibid.*, 1913, **35**, 864) show that aluminium hydroxide possesses acidic properties. There are, however, several other methods by means of which the acidity of aluminic acid can be determined. Thus, stable solutions of ammonium aluminate investigated physico-chemically prove the acidic function of aluminium hydroxide most distinctly, and these results agree with those obtained from sodium aluminate solutions, which will be considered first.

1. *Electrometric Titration of Sodium Hydroxide Solutions with Aluminic Acid.*

(a) *Conductivity Measurements.*—To dilute solutions of sodium hydroxide, small amounts of metallic aluminium were added, and the gradual decrease of conductivity was observed. The solutions were prepared by the action of pure sodium amalgam on conductivity water and kept in hard-glass bottles, into which weighed quantities of aluminium were introduced. After dissolution, the aluminate solutions were transferred through air-tight joints into conductivity cells with blank platinum electrodes. Atmospheric carbon dioxide was excluded by means of soda-lime tubes.

The metal used contained Al=98.2, Cu=0.94, Fe=0.63 per cent.

The results of the first set of measurements, carried out in a thermostat at 25°, are:

In 0.0422*N*-sodium hydroxide.

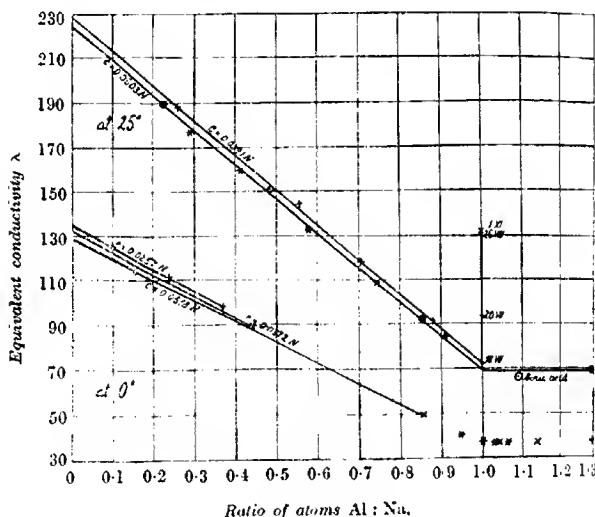
Gram-atoms of Al dissolved per litre.	Specific conductivity K. 10 <sup>3</sup> .	$\lambda_{OH} - \lambda_{Al} = \frac{1000 \Delta K}{\Delta C}$ .
0	9.595	—
0.00314	9.124	150
0.00507	8.792	158
0.00778	8.380	158
0.00902	8.145	160
0.01209	7.706	156
0.01411	7.347	158

In 0.0257*N*-sodium hydroxide.

0	5.871	—
0.00259	5.463	157
0.00607	4.934	154
0.00943	4.338	162

The single solutions remained stable, showing no change in conductivity during many days. The difference of mobilities of the hydroxyl ion,  $\lambda_{OH^-}$ , and the aluminate anion,  $\lambda_{AlO_4^-}$ , is calculated as  $1000 \frac{\Delta K}{\Delta C}$  — where  $\Delta C$  denotes the increase of aluminium in solution and  $\Delta K$  the corresponding decrease of specific conductivity. The mean value, 158, gives  $\lambda_{AlO_4^-} = 38$ ,  $\lambda_{OH^-}$  being taken as 196.

In the figure is shown the decrease of conductivity due to larger amounts of aluminium dissolved. The conductivity falls regularly with increasing concentration of aluminate, the slope remaining constant when the ratio of gram-atoms Al:Na is 1:3 or 1:2,



indicating that no formation of a salt of tri- or di-basic aluminate acid takes place. When, however, the ratio comes to 1:1, spontaneous decomposition of the solution occurs, during which crystalline aluminium hydroxide separates out, and the conductivity increases in the manner described by Slade and Polack (*Trans. Faraday Soc.*, 1914, **10**, 150).

In order to show that the decrease of conductivity effected by the dissolution of aluminium in alkali is not due to complex ionic "micelles," cryoscopic measurements were also carried out. To investigate how far the neutralisation of alkali by aluminate acid, the acidity of which might be questioned, differs from the action

of a recognised acid, such as boric acid, parallel experiments were made with the two acids.

The results, which are also plotted in the figure, were as follows:

In 0.05034*N*-sodium hydroxide.

Al in gram- atoms.	B(OH) <sub>3</sub> in gram- molecules.	Molec. cond.	$\Delta T$ .		$i = \frac{\Delta T}{1.86 \cdot C}$
			A.	$\Delta T$ .	
0	0.0112	224.7	189.6	0.170°	1.82
0.0144	—	177.0	—	0.176°	1.88
0.0206	—	159.0	—	0.183°	1.95
—	0.0243	150.9	—	0.176°	1.88
0.0296	—	132.3	—	0.186°	1.99
0.0375	—	108.2	—	0.179°	1.91
—	0.0430	92.8	—	0.180°	1.92
0.0439	—	84.5	—	0.174°	1.86
0.0503	—	79.7	—	0.179°	1.91
decomposes	0.0652	—	69.5	0.192°	2.05
—	0.0806	—	69.3	0.109°	2.12

The depression of freezing point,  $\Delta T$ , first slightly increases, reaching a maximum for solutions half saturated with aluminium hydroxide. This indicates that a monobasic aluminate is formed, which is slightly more dissociated than the pure alkaline solution. The boric acid, being soluble, shows a continual increase in osmotic pressure, as evident from van't Hoff's coefficient,  $i$ ; however, the changes in conductivity are in both cases identical.

To prevent the spontaneous decomposition of aluminates, it has been found necessary to work at 0°.

Since, however, the action of alkaline solutions on metallic aluminium ceases when the atomic ratio 1:1 is reached, amalgamated aluminium had to be added, in order to bring some more aluminium hydroxide in the nascent state into the solution. The amalgamation was effected by immersion in a solution of mercuric chloride; the amalgamated foil was then thoroughly rinsed with distilled water and introduced into the solution, which was kept in ice. At this temperature, the solutions were stable even when containing an excess of aluminium hydroxide. The conductivity of saturated 0.0257*N*- and 0.0372*N*-sodium hydroxide solutions was 36.8, and remained constant; only very slow increase could be observed when crystalline aluminium hydroxide was added.

The results are plotted in the figure. From the decrease of conductivity, again, the ionic mobilities at 0° were calculated; the mean difference of  $\lambda_{OH} - \lambda_{Al}$  is 104, which gives  $\lambda_{Al} = 14$ , when  $\lambda_{OH}$  is taken as 117.7 (Kohlrausch, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1026).

The important observation at 0°, namely, that the conductivity of aluminate solutions remains constant when the atomic ratio of Al:Na increases above 1:1, shows that there exists a definite saturation of one hydroxyl ion by one molecule of aluminium hydroxide, just as in the case of boric acid or (according to Kohlrausch, *Zeitsch. physikal. Chem.*, 1893, **12**, 782) of silicic acid. Judging from the phenomenon of spontaneous hydrolysis, during which aluminium hydroxide separates out, the action between the hydroxyl ion and the molecule may be regarded as addition rather than as neutralisation of the few hydrions due to the very sparingly soluble ortho-aluminic acid. The formation of meta-aluminic acid,  $\text{AlO}_2\text{H}$ , in solution cannot be expected, since the hydroxide,  $\text{Al}(\text{OH})_3$ , does not lose water below 130°.

(b) *Measurements of Electromotive Force.*—The decrease of hydron concentration effected by the addition of alkali to solutions of aluminium salts has been measured by Blum and Hildebrand (*loc. cit.*) by means of the potential of a hydrogen electrode. However, owing to the presence of aluminium salt and crystalline hydroxide, these measurements cannot be used for an exact determination of acidity. The same is the case with the experiments recently described by Fricke (*Zeitsch. Elektrochem.*, 1920, **26**, 129), from which no definite conclusion can be drawn, owing to the presence of finely divided aluminium hydroxide formed on hydrolysis in most concentrated alkali aluminate solutions. In the following experiments, the indicator of the hydron concentration was the mercuric oxide electrode. This electrode was filled with a solution of sodium hydroxide (according to Donnan and Allmand, T., 1911, **99**, 845), and was gradually neutralised by the addition of weighed quantities of aluminium. The electrodes and the solutions were kept at 25.0°. Single measurements were carried out in each case four to six days after the dissolution of the aluminium. The electrodes were measured against a normal calomel electrode, the diffusion potential being eliminated by a saturated solution of potassium chloride.

In this way, the results on p. 1017 were obtained at 25.0° for the cell.  $C_{\text{Al}}$  denotes the amount of gram-atoms of aluminium dissolved per litre; "E calculated" was obtained from the potential, -0.1774 volt, of the *N*-sodium hydroxide-mercuric oxide electrode by means of the formula

$$E = -0.1774 - 0.0591 \log_{10} [C_{\text{NaOH}} - C_{\text{Al}}].$$

It is the value which would be obtained if a strong acid in the amount  $C_{\text{Al}}$  were added. The first solution decomposed before saturation was reached. The measurements made with the second

Hg   (HgO solid) NaOH solution				saturated	N-calomel
				KCl	electrode
with 0.05417 <i>N</i> -NaOH.					
<i>C</i> <sub>Al</sub>	<i>E</i> observed in volt.	<i>E</i> calculated	<i>C</i> <sub>Al</sub>	<i>E</i> observed in volt.	<i>E</i> calculated
-- Nov. 20th	-0.1022	-0.1029	0.00505	-0.0779	-0.0780
0.0144	-0.0973	-0.0950	0.0102	-0.0690	-0.0681
0.0183	-0.0920	-0.0923	0.0157	-0.0581	-0.0568
0.0284	-0.0851	-0.0840	0.0183	-0.0356	-0.0305
0.0397	-0.0703	-0.0694	0.020	-0.0078	+0.010
0.0542 Dec. 20th decomposed	—	—	0.022	+0.0155	—
Dec. 31st	-0.0720	—	Jan. 6th	+0.0140	—
Jan. 2nd	-0.0820	—	Jan. 7th	+0.0140	—
" 6th	-0.0865	—	Jan. 8th decomposed	—	—
" 7th	-0.0870	—	—	—	—
" 11th	-0.0862	—	—	—	—
" 14th	-0.0857	—	—	—	—

solution, however, show that the solubility product of aluminic acid has been reached, since no appreciable change of potential took place when the number of aluminium atoms in solution exceeded that of sodium atoms.

The solubility product of aluminic acid is therefore

$$K_a = [Al'] \cdot [H^+] = \frac{C_{NaOH} \cdot K_w}{[OH^-]},$$

where  $K_w$  denotes the ionic product of water and  $C_{NaOH}$  the concentration of the sodium hydroxide solution, which for complete saturation becomes equal to the concentration of aluminic acid anions, denoted by  $[Al']$ .

Thus

$$0.0591 \log_{10} \frac{C_{NaOH}}{[OH^-]} = 0.015 + 0.0779 = 0.093 \text{ volt},$$

$$\frac{C_{NaOH}}{[OH^-]} = \frac{[Al']}{[OH^-]} = 37.3,$$

hence  $K_a = 37.3 \times 10^{-14}$  at 25°.

Similarly, the value of the solubility product of aluminic acid after spontaneous hydrolysis can be obtained from measurements of the first solution,

$$0.0591 \log_{10} \frac{C_{OH^-}}{[OH^-]} = -0.087 + 0.102 = +0.015 \text{ volt},$$

$$\frac{C_{OH^-}}{[OH^-]} = 1.795,$$

where  $C_{OH^-}$  denotes the concentration of hydroxyl ions in the pure sodium hydroxide solution, and is equal to  $0.054 \times 0.90N$ , this solution being ionised to the extent of 90 per cent.

Hence  $[OH'] = 0.0272$ . The concentration of the aluminate

anions,  $[\text{Al}']$ , is then equal to  $0.0542 - 0.0272 = 0.0270N$ , from which it follows that the solubility product of aluminic acid in the presence of crystalline aluminium hydroxide is

$$K_s' = \frac{0.0270}{0.0272} \cdot 10^{-14} = 10^{-14}.*$$

From measurements of electromotive force, it is evident that alkali is neutralised by freshly formed aluminium hydroxide until the ratio of molecules becomes 1:1, and that this neutralisation proceeds almost quantitatively, so that only a very small part, if any, can be present as colloidal alumina.

## II. Ammonium Aluminate.

The solubility of aluminium hydroxide in aqueous ammoniacal solutions is usually described as variable, depending on the time and way of precipitation. Thus Archibald and Habasian (*Trans. Roy. Soc. Canada*, 1918, **11**, 1) found analytically several hundreds per cent. of alumina in dilute ammoniacal solutions, whereas Renz (*Ber.*, 1903, **36**, 2751) obtained higher solubility in precipitating solutions of barium aluminate with ammonium sulphate. If, however, amalgamated aluminium is dissolved in ammonia, regular and well-defined neutralisation takes place, and still higher solubility is reached, as is evident from the following experiments, consisting of conductivity, cryoscopic, and analytical determinations.

### Measurements at 25°.

An ammoniacal solution of concentration  $C_{\text{NH}_3} = 0.117N$ , prepared by distilling pure ammonia into conductivity water out of contact with the atmosphere, showed the specific conductivity  $K = 3.900 \times 10^{-4}$  mho. After some amalgamated aluminium had dissolved in it, the conductivity increased to  $K' = 5.029 \times 10^{-4}$ , indicating that ammonium salt was formed, the concentration of which can be calculated as follows.

Knowing the equivalent mobility of aluminate anion,  $\lambda_{\text{Al}'} = 38$ , further  $\lambda_{\text{NH}_4} = 196$  and  $\lambda_{\text{OH}'} = 70.4$ , we have

$$1000 K' - 70.4[\text{NH}_4'] + 196[\text{OH}'] + 38[\text{Al}'].$$

Since, further,

$$[\text{NH}_4'] = [\text{OH}'] + [\text{Al}'] \quad \dots \quad (1)$$

$$1000 K' - 108.4[\text{NH}_4'] + 158[\text{OH}'].$$

\* Slade (*loc. cit.*) previously found the solubility product of the dried crystalline hydroxide to be  $0.37 \times 10^{-14}$  at 25°.

According to the law of mass action, which holds in the case of ammonia,

$$C_{\text{NH}_3} \cdot k = [\text{NH}_4^+] \cdot [\text{OH}^-] = \left( \frac{1000 K}{\lambda_{\text{NH}_4^+} + \lambda_{\text{OH}^-}} \right)^2 = \frac{(1000 K)^2}{266^2} \quad \dots \quad (2)$$

From the last two equations we obtain

$$[\text{NH}_4^+] = \frac{1000 K' + \sqrt{(1000 K')^2 - 4 \times 158 \times 108.4 \times (1000 K)^2 \cdot 1/266^2}}{2 \times 108.4}$$

as well as expressions for  $[\text{OH}^-]$  and  $[\text{Al}']$ .

The observed values of  $K$  and  $K'$  given above lead to  $[\text{NH}_4^+] = 0.00281N$  and  $[\text{Al}'] = 0.00155$  gram-molecule of aluminium hydroxide per litre.

Simultaneously, the increase of osmotic pressure, due to the formation of ammonium salt, has been determined by the lowering of freezing point of the ammoniacal solution, and was found to be  $0.226 \pm 0.001^\circ$ , against  $0.220^\circ$  of the pure solution. This change corresponds with an increase in concentration from  $0.118N$  to  $0.121N$ , agreeing with the conductivity results, from which the sum of the concentrations of molecules and ions is  $0.118$  for the pure solution and  $0.120$  for the solution containing aluminium hydroxide.

Further, fresh quantities of amalgamated aluminium were added to this solution, and readings were continued until the conductivity ceased to rise. The following results were obtained:

$C_{\text{Al}}$ concen- tration	specific con.	$K$					
		ductivity observed.	$[\text{Al}']$ calculated.	$[\text{NH}_4^+]$ calculated.	$\Delta T$ observed.	$\Delta T$ observed.	$C_{\text{NH}_3} +$ $[\text{NH}_4^+]$
of Al added.							
—	$3.900 \times 10^{-4}$	—	—	0.00146	$0.220^\circ$	0.118	0.118
0.0040	5.029	—	0.00155	0.00281	$0.226^\circ$	0.121	0.120
0.0060	6.662	—	0.00520	0.00559	$0.229^\circ$	0.123	0.123
0.0088	9.594	—	0.00823	0.00849	$0.231^\circ$	0.124	0.125
0.0129	9.45	—	—	—	$0.228^\circ$	—	—
0.016	9.2	—	—	—	—	—	—
decom- poses	3.910	—	0.00117	0.00216	—	—	—

From the solutions saturated with aluminium hydroxide, the ratio  $[\text{Al}']:[\text{OH}'] = \frac{0.000823}{0.000253}$ , which gives the ionic product  $[\text{Al}'] \cdot [\text{H}'] = 32.5 \times 10^{-14}$ . (From electromotive-force measurements,  $37.3 \times 10^{-14}$  was obtained.)

These solutions, however, were not stable; some hours after saturation has been reached, crystalline aluminium hydroxide separated out (consisting of microscopic crystals), and the conductivity fell to a value  $K' = 3.910 \times 10^{-4}$ , which remained constant.

Calculations of the solubility product,  $K'_a$ , from this reading give  $0.00117 \times 10^{-14} = 1.18 \times 10^{-14}$ . During this experiment, the walls of the cell and the electrodes were covered with the crystalline hydroxide. A fresh solution of pure ammonia in conductivity water ( $C_{NH_3} = 0.2237$ ,  $K = 0.5380 \times 10^{-3}$ ) was introduced into this cell and allowed to dissolve some of the crystalline hydroxide. After several days, the conductivity rose to  $K' = 0.5405 \times 10^{-3}$ , and remained constant. Again from  $K$  and  $K'$  the solubility product of aluminic acid in the presence of crystalline hydroxide follows  $K'_a = 1.23 \times 10^{-14}$ .

In order to determine analytically the amount of aluminium hydroxide which remains in the solution after the spontaneous hydrolysis, the saturated ammoniacal solutions were allowed to decompose at  $25.0^\circ$  and kept in the thermostat for several days. After a week, the solutions were filtered (in absence of carbon dioxide) into a platinum dish and evaporated. The results were as follows:

$C_{NH_3}$ .	Milligrams of $Al_2O_3$ in 100 grams of solution.	$[Al']$ .	$K'_a$ .
0.765 N.	18.1, 19.3	0.00366	$1.56 \times 10^{-14}$
0.523 "	14.6	0.00289	$1.44 \times 10^{-14}$
0.160 "	7.2, 7.6	0.00145	$1.27 \times 10^{-14}$

The constant  $K'_a$  was obtained in the following way.

From the equations (1), (2), and  $\frac{[Al']}{[OH']} = K'_a$  it follows on elimination, that

$$[Al'] = \sqrt{\frac{k \cdot K_a \cdot C_{NH_3}}{1 + K_a}} = k' \sqrt{C_{NH_3}},$$

from which  $K'_a$  can be calculated. These values are, however, not quite constant, decreasing slightly with decreasing concentration.

#### Measurements at $0^\circ$ .

Like the alkaline solutions of aluminium hydroxide, the ammoniacal solutions were also found to be quite stable at  $0^\circ$ . These solutions were prepared in the following way. To ammoniacal solutions carefully cooled in ice, amalgamated aluminium was added in a quantity sufficient to saturate the solution. The saturation was ascertained by conductivity readings, which first showed a steady increase, and after two days remained unchanged, although the dissolution of aluminium still proceeded.

TABLE I.  
Calculated from the values  $K$  and  $K'$ .

Concentration of ammonia. $C_{NH_3}$ .	Observed conductivity of the pure solution. $K \cdot 10^4$ .	Calculated from the values $K$ and $K'$ .				$Mg$ . of $Al_2O_3$ in 100 grams of solution analytically determined.
		$[OH^-]$ .	$[Al^+]$ .	$K_n = [OH^-] \cdot K'$ .	$Mg$ . of $Al_2O_3$ in 100 grams of solution.	
0.4117	0.3670	0.052	0.0192	0.000285	0.0189	106.
0.2237	0.2835	0.7894	0.0144	0.000227	0.0141	103.
0.1592	0.2270	0.6773	0.01238	0.000169	0.0122	73.1.
0.1028	0.1866	0.5519	0.01008	0.00016	0.00992	62.4.
0.0601	0.1467	0.3692	0.00668	0.000131	0.00655	—
0.0444	0.1292	0.3272	0.00592	0.000114	0.00580	—
0.0300	0.1037	0.2670	0.00486	0.000746	0.00479	—
0.0283	0.1002	0.2634	0.00453	0.000689	0.00449	—
0.00060	0.0265	0.0272	—	—	29.6	25.8.
$Q$	$Q^*$ conductivity water	0.0020	0.0010	—	—	—

Several days after the constant conductivity was attained, the solutions were filtered and analysed. The results are given in table I (p. 1021).

In solutions above 0.5*N* there was a too vigorous evolution of hydrogen, which carried off some ammonia and caused less solubility. Below 0.5*N*, however, the solutions showed great constancy. The mobilities of the ions  $\text{NH}_4^+$  and  $\text{OH}^-$  were taken as 39.3 and 117.7 respectively (Kohlrausch, *loc. cit.*), and the mobility of the aluminate ion,  $\lambda_{\text{Al}^3}$ , as 14.

The solutions could be easily filtered. That no colloidal hydroxide passed through the filter is evident from experiments with conductivity water, in which amalgamated aluminium was allowed to dissolve for several days, and which consequently contained much of the hydroxide, yet after filtration and evaporation left no measurable residue. The formation of aluminium hydroxide in pure water causes a decrease in conductivity.

The last two columns of table I show the close agreement between the conductivity and analytical results. The rather less solubility observed in more dilute solutions is probably due to minute quantities of carbon dioxide in conductivity water.

Some freezing-point determinations were also carried out, for example:

$C_{\text{NH}_3}$ .	$[\text{NH}_4^+]$ .	$\Delta T$ .	$\Delta T'$ .	$\Delta T'$ .
0.1028 <i>N</i>	0.0101	0.189°	0.210°	0.186
0.0601 <i>N</i>	0.0067	0.109°	0.120°	0.113

where  $\Delta T$  and  $\Delta T'$  denote the depression before and after the dissolution of aluminium. It will be observed that the concentration calculated from the depression  $\Delta T'$  (last column) is equal to the sum of molecules and ions,  $C_{\text{NH}_3} + [\text{NH}_4^+]$ , exerting the osmotic pressure. It is evident that no complex compounds of ammonia and aluminium hydroxide are formed, since the amount which exists in solution never exceeds that theoretically required for neutralisation.

The freshly formed aluminium hydroxide microscopically examined appears granular and shows the metallic structure of aluminium.

### III. *The Constitution of Aluminic Acid.*

In the experiments described above it is shown that at the ordinary temperature sudden change in aluminate solutions occurs, during which a large part of the dissolved aluminium hydroxide separates out in crystalline form, the ratio  $[\text{Al}^3]:[\text{OH}^-]$  reaching after considerable time the value 1.5—1.1. Similar values can

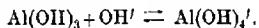
be obtained from final conductivities acquired after the spontaneous decomposition, assuming that the aluminate ion is the same as in solutions before the decomposition.

Thus at 25° in 0·0391*N*-sodium hydroxide, four months after the decomposition, the final molecular conductivity,  $\lambda=133\cdot 1$ , was observed; this is the conductivity of 0·0391*N*-sodium hydroxide when containing aluminium hydroxide dissolved in the ratio  $[\text{Al}^3]:[\text{OH}^-]=1\cdot 5$  before the decomposition. Hence

$$K'_a = 1\cdot 5 \times 10^{-14}.$$

Similarly, from 0·0422*N*-sodium hydroxide, after one month,  $\lambda=116\cdot 6$ ,  $K'_a = 1\cdot 8 \times 10^{-14}$ , and from 0·0257*N*-sodium hydroxide, after three weeks,  $\lambda=125\cdot 9$ ,  $K'_a = 1\cdot 7 \times 10^{-14}$ . Physical properties as well as analytical composition of solutions before the decomposition, were found identical with the properties of solutions of equal conductivity after the decomposition.

The supersaturation phenomena suggest that the compound formed by interaction between one molecule each of sodium hydroxide and aluminium hydroxide is the additive compound,  $\text{NaOH} \cdot \text{Al}(\text{OH})_3$ , which can be regarded as the sodium salt of aquo-aluminic acid,  $\text{H}^+[\text{Al}(\text{OH})_4]'$ , as suggested by Pfeiffer (*Ber.*, 1907, **40**, 4036). The process in the solution is therefore the following one: the hydroxyl ion joins the freshly precipitated molecule of aluminium hydroxide, and forms the anion of the aquo-aluminic acid, thus:



The anions,  $\text{Al}(\text{OH})_4'$ , joining hydrons form partly the very sparingly soluble acid,  $\text{HAl}(\text{OH})_4$ , the ionic product of which is  $77 \times 10^{-14}$  at 0°\* and  $35 \times 10^{-14}$  at 25°. (From these two constants, the heat of electrolytic dissociation of aquo-aluminic acid, calculated by means of van't Hoff's isochore, is 4900 cal.) In time, some of the aquo-aluminic acid decomposes by heat or traces of carbon dioxide, forming the ortho-hydroxide, the particles of which grow until they reach such an insolubility that the constant  $K_a$  of the aquo-aluminic acid becomes too large for the mass action of the above equation, according to which  $[\text{Al}(\text{OH})_3] = k \cdot K_a$ .

Consequently, the above reaction must proceed in the reverse direction until all solid aquo-aluminic acid disappears, which causes the sudden growth of crystals of aluminium hydroxide and extensive hydrolysis of the solution.

It was observed that the addition of crystalline hydroxide to a solution of aluminate also causes spontaneous hydrolysis.

\* According to Noyes' numbers (*Zeitsch. Physikal. Chem.*, 1910, **73**, 1),  $K_a$  at 0° is 0·11  $K_a$  at 25°.

At higher temperatures, the two solid phases, namely, the aquo-aluminic acid and aluminium hydroxide, cannot co-exist, but at 0° their transition temperature seems to be reached.

The crystalline aluminates furnish further evidence for the aquo-aluminates, which are fully hydrated (Werner, "Neuere Anschauungen," 1920, 4th ed., p. 126), and lose water in the same manner as aluminium hydroxide itself (Beckmann, *J. pr. Chem.*, 1882, [ii], 26, 385). Hydroxyl groups, which, according to Hantzsch's researches (*Ber.*, 1917, 50, 1422), never split off an acidic hydron, are all only basic in aluminium hydroxide. The acidity of this compound consists in the formation of additive compounds with alkalis.

The close resemblance of boric and aluminic acids (see figure) suggests that boric acid also forms aquo-salts, which is seen most markedly in the cases of borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , and lithium aluminato,  $\text{Li}_2\text{Al}_4\text{O}_7 \cdot 11\text{H}_2\text{O}$  (Allen and Rogers, *Amer. Chem. J.*, 1900, 24, 304), which are analogous aquo-salts of the type  $\text{M}^{\text{I}}\text{OH} \cdot \text{M}^{\text{III}}(\text{OH})_3 + \text{HOH} \cdot \text{M}^{\text{III}}(\text{OH})_3$ .

#### Appendix.

In this and in a previous paper (this vol. p. 11) the basigenic and acidigenic character of aluminium has been investigated from the point of view of the ionic splitting of its compounds in aqueous solutions. According to Abegg's theory of electroaffinity, basic or acidic properties of the hydroxide should be in close connexion with the electrolytic potential of the metal. However, in the case of aluminium, a metal of high position in the electro-potential series (E.P. = -1.34 volt,  $\text{H} = 0$ ; compare this vol., p. 27), this forms a hydroxide of feebly basic properties (the ionic product of basic splitting is  $10^{-33}$ ; compare this vol., p. 20), and at the same time of distinctly acidic character. The chloride, on the other hand, is very soluble and largely ionised, resembling in this respect the alkali haloids.

Obviously, Abegg's idea, that the electrolytic potential might be a measure of basicity, is not quite sound. There are heavy metals of more positive potential, such as silver, thallium, and lead, the hydroxides of which are fairly strong bases, and light metals of more positive potential, for instance, aluminium and zinc, of feebly basic hydroxides.

It seems that, besides the electron affinity, which represents the ease of escape of a valency electron from the atom, also the mass of the ion influences the basicity of the oxide and, in general, the ionisation of the compound. Thus Bektev's rule (*Phil. Mag.*,

1865, [iv], 31, 306), according to which the stability of a compound is the greater the more equal are the equivalent weights of the components, might be extended for ionisation processes.

We may therefore expect that a compound will ionise the easier the greater the difference in polarity (in the electrolytic potential) of the constituting ions and the more unequal their masses. Aluminium hydroxide is least, fluoride more, chloride, bromide, iodide most of all, ionised.

The acidity seems to depend, however, in general on the equivalent volume of the oxide, in that a small equivalent volume is accompanied by acidic properties, provided the basicity is feeble. Thus the small equivalent volume of alumina (4.1, which, next to that of glucina, is the least of all oxides) is connected with the acidity, developed in spite of the high position of aluminium in the potential series.

*Summary.*

(1) Electrometric measurements show that aluminium hydroxide neutralises alkalis as a monobasic acid. The mobility of alumination is 38 at 25° and 14 at 0°.

(2) Stable solutions of ammonium aluminate were obtained, for which the law of mass action holds good.

(3) The ionic product of aluminic acid is  $35 \times 10^{-14}$  at 25° and  $7.7 \times 10^{-14}$  at 0°; in the presence of crystalline aluminium hydroxide it is  $1.5 \times 10^{-14}$  at 25°.

(4) Evidence is adduced that aluminates are additive compounds of the type  $M'[Al(OH)<sub>4</sub>]<sup>1-</sup>$ , that is, salts of aquo-aluminic acid,  $H'[Al(OH)<sub>4</sub>]<sup>1-</sup>$ .

(5) The relation existing between the basicity, acidity, and the electrolytic potential is discussed.

I take this opportunity of offering my sincere thanks to Prof. B. Brauner for his helpful interest and encouragement in this work.

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**CXIV.—*The Nature of the  $\alpha$ -Ferricyanides and the  $\beta$ -Ferrocyanides.***

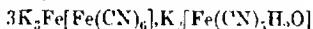
By SAMUEL HENRY CLIFFORD BRIGGS.

IT was found by Bennett (T., 1917, **111**, 490) that the  $\alpha$ - and the  $\beta$ -ferrocyanides (Briggs, T., 1911, **99**, 1019) are identical from a crystallographical point of view, and it therefore appeared probable that the  $\beta$ -ferrocyanides would prove to be mixtures of the ordinary ferrocyanides with a very small amount of highly-coloured impurity.

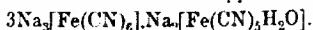
In view of Bennett's results, it was decided to make a further investigation of the two ferrocyanides, and also of the  $\alpha$ - and  $\beta$ -ferricyanides of Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413; see also Bellucci and Sabatini, *Atti R. Accad. Lincei*, 1911, [v], **20**, I; Piutti, *Ber.*, 1912, **45**, 1830; Hauser and Biesalski, *ibid.*, 3516; Wells, *Amer. Chem. J.*, 1913, **49**, 205). It is shown below that the  $\beta$ -ferricyanides are compounds of ferricyanide and aquopentacyanoferriate, whereas the  $\beta$ -ferrocyanides are mixed crystals of ferrocyanide and aquopentacyanoferroate, the amount of the latter being far too small to be detected by any known method of quantitative or qualitative analysis.

*The  $\beta$ -Ferricyanides.*

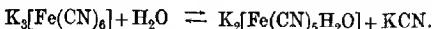
The analysis of the salt prepared according to the directions of Locke and Edwards pointed to the formula



rather than to Locke and Edward's formula,  $K_2Fe(CN)_6H_2O$ , but as it was scarcely possible to determine the exact formula of the double salt by analysis, synthetical means were used for this purpose. A simple method for the preparation of potassium aquopentacyanoferriate could not be devised, however, and recourse was therefore had to the sodium salt, which can readily be obtained by Hofmann's method (*Innalen*, 1900, **312**, 1). It was found that a solution of this salt with three and a-half molecular equivalents of sodium ferricyanide was precipitated at once with bismuth nitrate, proving that free ferricyanide was present, whereas a solution containing two and a-half molecular equivalents of sodium ferricyanide did not give a precipitate after a week, and consequently did not contain free ferricyanide. The formula of sodium  $\beta$ -ferricyanide would therefore appear to be



The ferricyanides in solution appear to decompose to some extent, as shown by the equation



The potassium cyanide produced gives cyanide ions, and these are removed on addition of acids, owing to formation of the very slightly dissociated hydrogen cyanide. Acids therefore increase the velocity of the reaction towards the right. Alkalies and ammonia, on the other hand, decompose the aquopentacyanoferriate (compare Hofmann, *loc. cit.*), and cyanides convert the aquopentacyanoferriate into ferricyanide, thereby increasing the reaction towards the left.

These transformations are shown by the colour changes developed in solutions of potassium ferricyanide when the above-mentioned reagents are added, acids causing an intensification of colour, owing to increase of aquopentacyanoferriate, whereas alkalies, ammonia, and cyanides diminish the colour, owing to removal of the intensely coloured aquopentacyanoferriate.

When pure, bright orange-red potassium ferricyanide is recrystallised from a solution containing 2 or 3 per cent. of sodium aquopentacyanoferriate, garnet-red crystals are obtained, differing very much in habit from the orange-red crystals of the pure salt. These garnet-red crystals are analogous to potassium  $\beta$ -ferrocyanide, as shown below.

There is thus an explanation of the very deep colour of many preparations of potassium ferricyanide made by oxidising potassium ferrocyanide with chlorine, for not only does the chlorine oxidise the ferrocyanide, but it also decomposes the ferricyanide to some extent, according to the equation



as found by Cambi (*Gazzetta*, 1911, **41**, i, 157). The deeply coloured crystals are therefore mixed crystals of potassium ferricyanide, and the double salt of ferricyanide and aquopentacyanoferriate ( $\beta$ -ferricyanide).

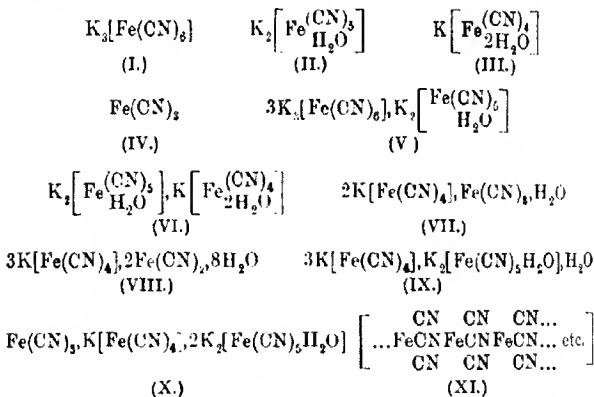
#### *The Action of Bromine on Potassium Ferricyanide.*

In view of the above-mentioned observations of Cambi, it appeared probable that the action of bromine on potassium ferricyanide would furnish a convenient method for the preparation of " $\beta$ -ferricyanide," and this expectation was realised, further evidence thus being provided for the constitution suggested above. Larger quantities of bromine gave a brownish-black colloidal substance of the formula **IX** or **X**, whilst with excess of bromine,

greenish-black, insoluble ferric cyanide was formed (compare Reynolds, T., 1888, 53, 769; Messner, *Zeitsch. anorg. Chem.*, 1895, 9, 126). A small quantity of a white solid sparingly soluble in hot water was produced, together with the ferric cyanide. The analysis of this substance suggested a polymeride of cyanic acid, but the amount was too small for complete identification.

### *The Action of Hydrochloric Acid on Potassium Ferricyanide*

The action of hydrochloric acid on potassium ferricyanide (I) has been studied beyond the stage of the formation of Locke and Edwards'  $\beta$ -ferricyanide (V). Although the acid successively removes the three molecules of potassium cyanide, with the final production of ferro cyanide (IV), it has not been possible to isolate potassium aquopentacyanoferrate (II) or the hitherto unknown diaquotetracyanoferrate (III). Not only are the compounds II and III extremely soluble in water and difficult to isolate in the crystalline state, but the compounds I, II, III, and IV have a pronounced tendency to combine with each other, with or without elimination of water molecules, to give the substances V, VI, VII, and X.



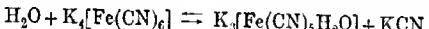
Although the formulae V--X are useful as showing the way in which the compounds are derived from potassium ferriyanide, it is probable that these substances are not simply double salts, but rather salts of highly complex anions containing several iron atoms and a correspondingly large number of cyanogen groups. Evidence for this view is obtained from the distinctive precipitation reactions of Locke and Edwards' salt, and also from the properties of

ferro cyanide, which is a highly insoluble salt with colloidal properties instead of a readily soluble substance, as would be expected from the simple formula IV. Ferro cyanide would therefore appear to be highly polymerised, possibly with each iron atom at the centre of a regular octahedron, a cyanogen group at each corner, and every cyanogen group united to at least two iron atoms. The simplest structure of this type is seen in the "chain" formula XI.

*The  $\beta$ -Ferrocyanides.*

Potassium  $\beta$ -ferrocyanide crystallises on cooling from a warm, saturated solution of the  $\alpha$ -ferrocyanide containing one part of sodium aquopentacyanoferroate (compare Hofmann, *loc. cit.*) per hundred parts of the ferrocyanide. The  $\beta$ -ferrocyanides are therefore mixed crystals of ferrocyanide and aquopentacyanoferroate, the amount of the latter being far too small to be detected by qualitative or quantitative analysis.

Since potassium  $\beta$ -ferrocyanide is formed when the  $\alpha$ -ferrocyanide is repeatedly recrystallised from water, it follows that the ferrocyanides in aqueous solution are in a state of equilibrium, as seen from the equation



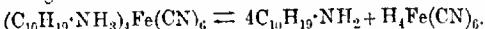
The effect of acids, alkalis, ammonia, and cyanides on this equilibrium is analogous to that described above in the case of the ferricyanides, and need not be referred to in detail. It is sufficient to say that a simple explanation is hereby provided for the various transformations mentioned in the former paper (T., 1911, 99, 1019).

The possibility that the  $\beta$ -ferrocyanides are  $\alpha$ -ferrocyanides containing a trace of a highly-coloured impurity was considered in the former paper, but as two *l*-menthylammonium ferrocyanides were obtained which differed considerably in specific rotation, it was concluded that the  $\alpha$ - and  $\beta$ -ferrocyanides were isomeric. The *l*-menthylammonium  $\alpha$ -ferrocyanide has  $[\alpha]_D^{25} - 42.4^\circ$  and the  $\beta$ -ferrocyanide  $[\alpha]_D^{25} - 28.5^\circ$ . Further, on adding a trace of acid to a solution of the  $\alpha$ -ferrocyanide in alcohol, the specific rotation was observed to fall from  $-40.9^\circ$  to  $-31.8^\circ$ .

The former preparation of *l*-menthylammonium  $\beta$ -ferrocyanide, was no longer available, but there can be no doubt from its properties, as previously described, that it contained aquopentacyanoferroate as well as ferrocyanide. Whether its low rotatory power was due to some change of the nature of racemisation in the *l*-menthylammonium groups or to the presence of some impurity cannot now be decided, and this point remains obscure. An ex-

planation of the fall in rotation of the *l*-menthylammonium  $\alpha$ -ferrocyanide on the addition of acid has been furnished by a study of quininium primary ferrocyanide. When the quininium salt was dissolved in alcohol or acetone, the specific rotation was found to rise for some days, and then become constant, the change being as much as  $20^\circ$  in some experiments. An examination of the product showed that ferricyanide was present, the salt having undergone oxidation by atmospheric oxygen dissolved in the solution. It was then observed that the preparation of *l*-menthylammonium ferrocyanide described in the former paper also underwent oxidation when its solution in alcohol was exposed to the air for some time, and from the residue pure *l*-menthylammonium ferricyanide was isolated.

This tendency of the ferrocyanides of substituted ammonium bases to undergo oxidation by atmospheric oxygen is probably the result of slight dissociation into base and acid, for example,



The addition of acid will increase the amount of the readily oxidisable hydrogen ferrocyanide, and thereby accelerate the change. This will account for the fall in rotation previously observed on the addition of acid to an alcoholic solution of *l*-menthylammonium  $\alpha$ -ferrocyanide. The solution used was dilute, and the amount of oxygen required to oxidise all the ferrocyanide present was very small, and would easily be provided by air dissolved in the liquid.

#### EXPERIMENTAL.

##### *Locke and Edwards' Potassium $\beta$ -Ferricyanide.*

The salt prepared according to the directions of Locke and Edwards (*loc. cit.*) was obtained as a yellowish-green solid. Its precipitation reactions agreed exactly with the observations of Locke and Edwards, but the analysis was not in accordance with their formula,  $K_3Fe(CN)_6 \cdot H_2O$ . They decomposed their salt with nitric acid, and for this reason, apparently, their figures for the iron content were too low, as it was found impossible during the present research to obtain complete decomposition when using nitric acid. On heating the salt with concentrated sulphuric acid, however, the complex was entirely destroyed. On diluting the product with a little water and carefully neutralising with ammonia, the double salt of potassium and ferric sulphates, which is practically insoluble in the presence of acid, could be readily dissolved on warming, and the analysis carried out in the usual manner.

	K.	Fe.	N.	H <sub>2</sub> O <sub>4</sub>
K <sub>3</sub> Fe(CN) <sub>6</sub> ·H <sub>2</sub> O .....	requires	33·78	16·08	24·21
Found .....		33·82	17·61	24·73
3K <sub>3</sub> Fe(CN) <sub>6</sub> ·K <sub>2</sub> [Fe(CN) <sub>5</sub> ·H <sub>2</sub> O] .....	requires	33·87	17·59	25·37
4K <sub>3</sub> Fe(CN) <sub>6</sub> ·K <sub>2</sub> [Fe(CN) <sub>5</sub> ·H <sub>2</sub> O] .....	"	34·23	17·46	25·41
5K <sub>3</sub> Fe(CN) <sub>6</sub> ·K <sub>2</sub> [Fe(CN) <sub>5</sub> ·H <sub>2</sub> O] .....	"	34·47	17·37	25·43
				0·93 { per cent.}

When heated to 210°, the salt underwent further decomposition, with loss of cyanogen. The analysis points to a compound of aquopentacyanoferriate and ferricyanide rather than to a salt of the formula K<sub>3</sub>Fe(CN)<sub>6</sub>·H<sub>2</sub>O, but it is scarcely possible to determine the exact formula of the double salt by quantitative analysis alone. In agreement with the analytical data, it was found that the compound gave the characteristic reaction for iron pentacyano-derivatives described by Hofmann (*loc. cit.*), for when its solution was treated with hydroxylamine hydrochloride rendered alkaline with sodium hydroxide and heated, it became deep golden-yellow with copious effervescence.

An attempt was made to determine the constitution by titration with potassium cyanide until the colour of aquopentacyanoferriate had disappeared, but no definite end-point was obtained, showing that potassium ferricyanide has a tendency to decompose in solution according to the equation



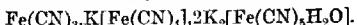
During the titration of the  $\beta$ -ferricyanide with potassium cyanide, it was noted that the solution, on keeping, deposited a little Prussian-blue, in agreement with the observations of Hauser and Biesalski (*loc. cit.*).

*The Action of Bromine on Potassium Ferricyanide.*

*Preparation of Locke and Edwards' Salt.*—Ten grams of potassium ferricyanide were dissolved in 50 c.c. of water, and 1·4 grams of bromine were added to the cold solution. The mixture was kept in a stoppered bottle, the bottle being occasionally shaken. After three days, the solution no longer contained free ferricyanide, as shown by the absence of a precipitate with bismuth nitrate. On precipitating with 150 c.c. of alcohol (90 per cent.), the salt was obtained as a greenish-brown, crystalline dihydrate (Loss over sulphuric acid in a vacuum=2·61. Calc.: 2·75 per cent.). Analysis of the dehydrated salt gave K=34·04; Fe=17·64; N=24·86. 3K<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>K<sub>2</sub>[Fe(CN)<sub>5</sub>·H<sub>2</sub>O] requires K=33·87; Fe=17·59; N=25·37 per cent. When prepared in this manner, the compound was free from Prussian-blue, and therefore gave a

yellowish-white precipitate with stannic chloride. The salt also gave Hofmann's reaction for iron pentacyano-compounds.

*The Brownish-black Colloid,*

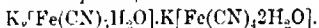


—Eight grams of bromine were added to a solution of 12 grams of potassium ferricyanide in 60 c.c. of cold water, and the mixture was kept in a loosely stoppered bottle at the summer temperature (20—25°). Some gas was evolved, and the solution, after changing colour to brown and then to violet, deposited a black jelly. After ten days, the mixture was poured into 200 c.c. of alcohol (90 per cent.), and the black solid collected and dried in the air. It was then powdered and washed on a filter with cold water until free from soluble impurities. The compound now increased greatly in volume, owing to absorption of water, and the jelly-like mass which resulted was analysed after drying in a vacuum over sulphuric acid until its weight was constant (Found: K=21.60; Fe=24.08; N=26.21. Calc.: K=21.79; Fe=24.90; N=26.55 per cent.).

The compound was soluble in hydrochloric acid, with production of a characteristic, greenish-blue colour. It dissolved in warm water to a dark brown, colloidal solution.

*The Action of Hydrochloric Acid on Potassium Ferricyanide.*

*The Bluish-violet Compound,*



—Ten grams of potassium ferricyanide dissolved in 20 c.c. of water were treated with 5 c.c. of hydrochloric acid (D 1.15) in an open flask immersed in water at 70—80° for forty minutes. The solution was allowed to remain overnight and filtered. The deep purple filtrate was then precipitated with two volumes of alcohol (90 per cent.). The semi-solid deposit was dissolved in a very small amount of water and precipitated with two volumes of alcohol, the process being repeated ten or twelve times until the alcoholic layer had a bluish-violet colour without any red or yellow tinge. The product was now dissolved in the smallest possible quantity of water, and a trace of Prussian-blue was removed by filtration. The filtrate was evaporated to dryness in a vacuum over sulphuric acid, leaving an extremely soluble, highly deliquescent, friable, black solid. Three and a-half grams were obtained from 35 grams of potassium ferricyanide (Found: K=23.70; Fe=21.69; N=24.00. Calc.: K=22.69; Fe=21.59; N=24.38 per cent.). At 160° one molecule of water was evolved, the loss in weight being 3.51 (Calc.: 3.48 per cent.).

*The Greenish-black Compound, 2K[Fe(CN)<sub>4</sub>]<sub>2</sub>Fe(CN)<sub>5</sub>H<sub>2</sub>O.*—

Twenty grams of potassium ferricyanide were dissolved in 40 c.c. of water, and 16 c.c. of hydrochloric acid (D 1.15) added. The mixture was heated at 55—60°, the solution being filtered every ten hours to remove the precipitated ferric cyanide. After the fourth filtration, only a small amount of ferric cyanide separated, and the acid reaction was very weak. The heating was continued a further twelve hours (fifty-two hours in all), and the cold solution was then precipitated with two volumes of alcohol (85 per cent.). The black, semi-solid deposit was purified by repeated solution in water and precipitation with alcohol (85 per cent.) at a room temperature of 20—25°, the quantities used being 15 c.c. of water and 30 c.c. of alcohol, once; 10 c.c. of water and 20 c.c. of alcohol, twice; 5 c.c. of water and 10 c.c. of alcohol, twice; and 5 c.c. of water and 15 c.c. of alcohol, three times. During the final stages of purification, the compound was obtained in the solid state, the yield of pure salt being half a grain. This was dissolved in a small quantity of water, evaporated to dryness over sulphuric acid, and weighed for analysis. On exposure for some weeks in a vacuum over sulphuric acid, it slowly evolved a molecule of water (Found: K=14.67; Fe=30.26;  $H_2O=3.00$ . Calc.: K=14.22; Fe=30.47;  $H_2O=3.28$  per cent.). The compound was deliquescent and very readily soluble in water to a greenish-black solution.

*The Dark Blue Compound,  $3K[Fe(CN)_4]_2Fe(CN)_2, 8H_2O$ .*—Forty grams of potassium ferricyanide dissolved in 80 c.c. of water were heated at 55—60° with 12 c.c. of hydrochloric acid (D 1.15). A further 32 c.c. of hydrochloric acid were added in quantities of 8 c.c. at intervals of twelve hours, the heating being continued for twelve hours after the last portion of acid had been added, or sixty hours in all.

The filtrate from the dark green precipitate (A) was greenish-blue (volume, 100 c.c.). One hundred and fifty c.c. of alcohol (85 per cent.) were added, and the viscous deposit was dissolved in 15 c.c. of water and filtered. The magnificent deep blue solution was precipitated with 45 c.c. of alcohol (85 per cent.), and the treatment repeated a few times, 15 c.c. of water and 45 c.c. of alcohol being used on each occasion at a room temperature of 20—25°. The salt was finally obtained as a deep indigo-blue powder free from white crystals of potassium chloride. When exposed over sulphuric acid in a vacuum for three weeks, it lost four molecules of water, and the weight thereafter remained constant [Loss=7.73. Calc.: 7.53 per cent. for a loss of  $4H_2O$  from  $3K[Fe(CN)_4]_2Fe(CN)_2, 8H_2O$ . The residue then gave K=13.19; Fe=31.52; N=25.96.  $3K[Fe(CN)_4]_2Fe(CN)_2, 4H_2O$  requires K=13.26; Fe=31.55; N=25.45 per cent.].

The green precipitate (A), after drying, had the composition

Fe: 2.78N: 0.05K:  $x$ H<sub>2</sub>O. It therefore consisted of a slightly decomposed ferric cyanide, which salt was shown by Messner (*loc. cit.*) to lose cyanogen with great ease. This decomposition explains the presence of ferrous iron in the deep blue compound.

The compounds represented by the formulae II to X are all intensely coloured.

Those compounds which had been subjected to prolonged treatment with alcohol in the course of purification gave an odour of isocyanides when decomposed with alkalis. This reaction may be due to the presence of a trace of the corresponding ethyl esters, and is significant in view of the results of Bellucci and Sabatini (*loc. cit.*).

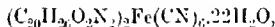
The compounds VI, VII, VIII, and X all give ferrocyanide as well as ferricyanide when decomposed by alkalis. It does not follow, however, that they all contain ferrous iron, since Messner has shown (*loc. cit.*) that compounds like cupric ferricyanide, Cu<sub>5</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>, behave in the same way.

*Quininum Primary Ferrocyanide.*

Four grams of potassium ferrocyanide in 200 c.c. of water were added with stirring to a solution of 16 grams of quinine monohydrochloride in 400 c.c. of water in the cold. After two days, the pure, white icosahydrate was collected, washed with water, and dried in the air. On dehydration over sulphuric acid in a vacuum, it rapidly lost 17H<sub>2</sub>O, and a further two molecules were evolved more slowly, the weight becoming constant after five weeks. The product was a hygroscopic, yellow monohydrate.

Analysis of the icosahydrate gave: Fe = 3.08; H<sub>2</sub>O = 18.12, 18.11. (C<sub>20</sub>H<sub>25</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>Fe(CN)<sub>6</sub>·20H<sub>2</sub>O requires Fe = 2.98; 19H<sub>2</sub>O = 18.27. The monohydrate gave C = 67.22, 67.46; H = 6.38, 6.64; Fe = 3.69, 3.75. Calc.: C = 67.42; H = 6.72; Fe = 3.65 per cent.

*Quininum secondary ferrocyanide,*



separated as a black solid, insoluble in all ordinary solvents from a solution of 5 grams of quinine bisulphate in 250 c.c. of water to which 2 grams of potassium ferrocyanide in 10 c.c. of water had been added (Found: Fe = 4.42. Calc.: Fe = 4.43 per cent.). On dehydration over sulphuric acid, the hemihydrate was obtained (Loss = 31.16; 21H<sub>2</sub>O requires 30.72 per cent.). Analysis of the hemihydrate gave: C = 62.86, 63.03; H = 5.83, 6.20. Calc.: C = 63.20; H = 6.07 per cent.

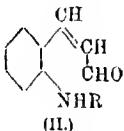
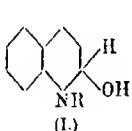
[Received, May 18th, 1920.]

CXV—*The Cyanine Dyes. Part II. The Synthesis of o-Aminocinnamylidenequinaldine Methiodide.*

By WILLIAM HOBSON MILLS and PERCY EDWIN EVANS.

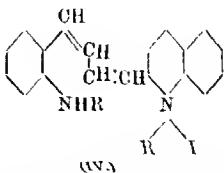
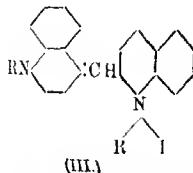
It has been generally recognised that in the formation of isocyanines by the action of alkalis on mixtures of a quinoline with a quinaldine alkyl iodide, a dominant part is played by the highly reactive  $\psi$ -bases to which the action of alkalis on a quinoline alkyl iodide is known to give rise.

Two views are held with respect to the constitution of these  $\psi$ -bases. In addition to the cyclic carbinol formula (I) suggested by Decker (*Ber.*, 1892, **25**, 3326), an open-chain alkylamino-



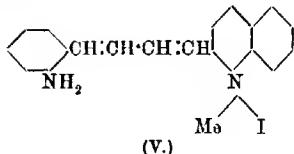
aldehyde formula (II) was proposed by Roser (*Annalen*, 1892, **272**, 221; 1894, **282**, 363), and was supported with additional experimental evidence by Gadamer (*Arch. Pharm.*, 1905, **243**, 2; 1908, **246**, 89) and Kaufmann and Strübin (*Ber.*, 1911, **44**, 80).

It was pointed out by W. König (*J. pr. Chem.*, 1912, [ii], **86**, 66) that the possibility that the quinolinium  $\psi$ -bases were to be represented by the second of these formulae made it necessary to take into account a corresponding constitution for the isocyanines. Accordingly, in place of the formula (III) which he had originally proposed (*J. pr. Chem.*, 1906, [ii], **73**, 100) for this class of dyes, he now suggested the open-chain formula (IV), and gave reasons for preferring it to the formulae which had previously been put forward.



With a view to obtain evidence which would bear on the constitution of the isocyanines, we undertook the synthesis of a com-

pound of a type almost identical with that represented by formula IV. This substance was *o-aminocinnamylidenequinaldine methiodide* (V), the structural formula of which only differs from König's butadiene formula for dimethylisocyanine iodide in that it contains an amino-group in place of a methylamino-group attached to the benzene nucleus in the ortho-position with respect to the butadiene chain.



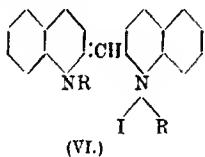
Meanwhile, the facts described in a preceding paper (Mills and Wishart, this vol., 579) were discovered. These showed definitely that the isocyanines do not possess an open-chain formula, and the chief object of these experiments was thus attained in another way; we think, however, that the synthesis and properties of *o-aminocinnamylidenequinaldine methiodide*, which in certain respects bears a distinct relationship to the dyes of the cyanine class, may still be of sufficient interest to be recorded.

The synthesis was effected in the following manner. *o*-Nitrocinnamaldehyde was heated with quinaldine and zinc chloride, when condensation took place, with the formation of *o-nitrocinnamylidenequinaldine*,  $\text{NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CH}\text{--CH}=\text{CH}\text{--C}_6\text{H}_5\text{N}$ . This was reduced with iron and acetic acid to the corresponding amino-compound, which forms deep reddish-brown mono-acid salts and di-acid salts, which are pale yellow and characterised by their sparing solubility.

To prepare the quaternary methiodide of this base, the amino-group was first protected by acylation. The acylamino-compound was then converted into its methiodide by heating with methyl iodide, and finally the acyl group was eliminated. Various acyl derivatives having been examined, the *formyl* compound was found to give the best results, and its *methiodide*, on hydrolysis with dilute hydrochloric acid, gave *o-aminocinnamylidenequinaldine methiodide* (V).

It proved to be a compound which forms deep reddish-brown solutions and crystallises in small, oblique-ended needles showing a dark olive-green metallic reflex; the crystals are strongly pleochroic, but almost opaque. Its strongly coloured aqueous solutions are at once turned pale yellow by the addition of mineral acids, evidently on account of the formation of di-acid salts. It

dyes wool, and especially silk, a beautiful rich reddish-brown, but the colour is surprisingly fugitive in daylight. Its absorption spectrum in the visible region, unlike the spectra of the *isocyanines*, which are characterised by a distinctive pair of bands, shows only general absorption in the violet and blue, which in more concentrated solutions extends as far as the orange. It has also no appreciable sensitising action on a gelatino-bromide photographic plate. Apart, therefore, from its instability towards light and its partial decolorisation by acids, it shows little analogy in properties to the *isocyanines*. At the same time, the fact should not be overlooked that, on account of the presence of the two ethylenic linkings in the butadiene chain, a compound of this structure should be capable of existence in four geometrically isomeric forms, only one of which is closely related in configuration to cyanine dyes, namely, those of the at present unknown  $\alpha$ - $\alpha$ -class (VI), the properties of which can, however, to some extent be inferred from those of the analogous compounds of the benzothiazole series prepared by Hofmann (*Ber.*, 1888, 21, 2262).



#### EXPERIMENTAL.

*o-Nitrocinnamaldehyde*.—We first prepared this substance by the method described by Diell and Einhorn (*Ber.*, 1885, 18, 2336), but as the process proved troublesome to carry out, we sought for some method of nitrating cinnamaldehyde by which the *o*-nitro-derivative could be more easily obtained. Experiments on nitration in the presence of acetic anhydride showed that the process could be conducted so that *o*-nitrocinnamaldehyde was the sole crystalline product.

A solution of 25 grams of nitric acid (D 1.50) in 50 grams of glacial acetic acid was dropped slowly, with frequent shaking, into an ice-cold solution of 50 grams of cinnamaldehyde in 200 c.c. of acetic anhydride. The solution was allowed to remain for two days at the ordinary temperature; dilute hydrochloric acid was then added and the mixture well shaken. Considerable heat was developed, and, on cooling, *o*-nitrocinnamaldehyde crystallised in almost colourless needles. By recrystallising once from alcohol, the compound was obtained pure in very pale yellow needles melting

at 127°. This method thus gives a very simple means of preparing *o*-nitrocinnamaldehyde, and although the yield is only 36 per cent. of the weight of cinnamaldehyde taken, it could probably be improved by further investigation of the process.

*o-Nitrocinnamylidenequinaldine*.—A mixture of *o*-nitrocinnamaldehyde (10 grams), quinaldine (8.1 grams), and zinc chloride (2 grams) was heated on the water-bath for five hours. The resulting crystalline mass was dissolved in hot acetone, and the solution, on cooling, deposited the pure condensation product in yellow rhombs melting at 149°. The compound dissolves readily in hot acetone or chloroform, sparingly in alcohol, benzene, or ether (Found: N=9.28.  $C_{19}H_{14}O_2N_2$  requires N=9.27 per cent.).

*p-Nitrocinnamylidenequinaldine*.—*p*-Nitrocinnamaldehyde (10 grams) and quinaldine (8.1 grams) were heated together on the boiling-water bath for ten hours. The product was dissolved in alcohol, the solution poured into water, and the yellow solid was collected and crystallised from acetone. Pure *p*-nitrocinnamylidenequinaldine was thus obtained in yellow needles melting at 185.5° (Found: N=9.25.  $C_{19}H_{14}O_2N_2$  requires N=9.27 per cent.).

*o-Aminocinnamylidenequinaldine*,



—An examination of the action of various reducing agents on *o*-nitrocinnamylidenequinaldine showed that the reduction could be carried out most conveniently by means of iron and acetic acid. The nitro-compound (10 grams) was dissolved in warm glacial acetic acid, the solution diluted with water, and excess of iron added. The mixture, which rapidly became a deep reddish-brown, was kept at 60° for two hours, and the excess of iron was then removed. On adding concentrated hydrochloric acid, the sparingly soluble yellow dihydrochloride of the new base was precipitated. It was collected, washed with concentrated hydrochloric acid, and decomposed with ammonia. On crystallising the base thus formed from aqueous alcohol, it was obtained in yellow needles melting at 135.5°. It is very readily soluble in alcohol or chloroform, moderately so in acetone, ether, or benzene, and practically insoluble in water (Found: C=83.3; H=5.9; N=10.2.  $C_{19}H_{16}N_2$  requires C=83.8; H=5.9; N=10.3 per cent.).

*o-Formylaminocinnamylidenequinaldine*,



—*o*-Aminocinnamylidenequinaldine was heated with excess of 90 per cent. formic acid under reflux on the sand-bath for three hours. After cooling, the mixture was diluted with water, rendered alkaline with ammonia, and the precipitated formyl derivative was

collected and crystallised from alcohol. It formed pale yellow needles melting at 185.5°. This compound is readily soluble in hot alcohol or chloroform, fairly so in acetone, and sparingly so in ether or benzene (Found: N=9.4.  $C_{29}H_{36}ON_2$  requires N=9.3 per cent.).

*o-Formylaminocinnamylidenequinaldine Methiodide.*—Formylaminocinnamylidenequinaldine (2 grams) was heated with methyl iodide (6 grams) in a sealed tube at 100° for three hours. The red mass obtained in this way crystallised from alcohol in dark red needles, which melted at 218°. The substance is soluble in hot water or alcohol, sparingly so in acetone or chloroform, and insoluble in ether or benzene (Found: I=28.7.  $C_{21}H_{19}ON_2I$  requires I=28.7 per cent.).

*o-Acetylaminocinnamylidenequinaldine,*



—The amino compound (10 grams) was heated for one hour on the water-bath with acetic anhydride (30 grams). The excess of acetic anhydride was then decomposed by heating with water, and the acetyl derivative precipitated by the addition of ammonia. It was collected and crystallised from aqueous alcohol, from which it separates in pale yellow needles melting at 179°. It is soluble in chloroform and dissolves very readily in alcohol. It is almost insoluble in ether, acetone, water, or benzene (Found: N=8.9.  $C_{19}H_{26}ON_2$  requires N=8.9 per cent.).

*Acetylaminocinnamylidenequinaldine Methiodide.*—The acetyl derivative (2 grams) was heated with methyl iodide (4 grams) in a sealed tube at 100° for three hours. The bright red contents of the tube were crystallised from water, and then recrystallised from alcohol. The methiodide obtained in this way consisted of bright red needles melting at 216—217° (Found: I=27.75.  $C_{22}H_{21}ON_2I$  requires I=27.85 per cent.).

It is soluble in water, alcohol, or acetone, sparingly so in chloroform, and insoluble in ether or benzene.

*Carboxymethylaminocinnamylidenequinaldine,*



—A solution of *o*-aminocinnamylidenequinaldine (2.5 grams) in dry chloroform was heated with methyl chloroformate (1 gram) under reflux for four hours. Water was added, and then ammonia until the red colour of the hydrochloride disappeared. The chloroform layer was separated, the chloroform evaporated, and the residue crystallised from alcohol. The compound formed lustrous, yellow plates melting at 175.5° (Found: N=8.5.  $C_{21}H_{15}O_2N_2$  requires N=8.5 per cent.).

This compound is readily soluble in hot alcohol or chloroform.

sparingly so in acetone, ether, or benzene, and practically insoluble in water.

*o-Aminocinnamylidenequininaldine Methiodide* (V).—This substance was obtained by the hydrolysis of its acyl derivatives, the reaction being most easily carried out with the formyl compound. Formylaminocinnamylidenequininaldine methiodide is readily hydrolysed by dissolving in hot water, adding a little concentrated hydrochloric acid, and boiling for twenty minutes. To ensure getting the iodide uncontaminated with chloride, potassium iodide was added to the mixture, and the greater part of the acid was then neutralised with ammonia, when a dark reddish-brown precipitate of the iodide was obtained. This was recrystallised from methyl alcohol to which a little aqueous potassium iodide had been added. The salt forms needles with a very dark olive-green lustre melting at 194.5°. It is very readily soluble in methyl alcohol, less so in ethyl alcohol or water, and sparingly so in acetone or chloroform. For analysis it was dried in a vacuum at 70° (Found: C=57.5; H=4.6; N=6.53; I=30.4, 30.8.  $C_{20}H_{19}N_2I$  requires C=58.0; H=4.6; N=6.76; I=30.7 per cent.).

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**CXVI.—The Isomerism of the Oximes. Part IX.  
2:4-Dinitrobenzaldoxime and Bromo-substituted  
Hydroxy- and Methoxy-benzaldoximes.**

By VERA WENTWORTH and OSCAR LISLE BRADY.

On the Hantzsch-Werner hypothesis, all substituted benzaldoximes should exist in two stereoisomeric forms. In a number of cases, however, all attempts to obtain the unstable isomeride have been unsuccessful (compare Brady and Dunn, T., 1916, 109, 667), but from a study of these cases there has emerged no underlying principle determining the non-existence of the second form other than the inhibiting effect of the hydroxyl group.

A number of other substituted benzaldoximes have now been investigated with a view to arrive at some generalisation.

The nitrobenzaldoximes all exist in two isomeric forms, and although 2:4-dinitrobenzaldoxime has been prepared (Sachs and Kempf, Ber., 1902, 35, 1234), its configuration has not been determined. It has been found to possess the *anti*-configuration by the preparation of its acetyl derivative and hydrolysis of this compound to the original oxime according to Hantzsch's method.

It does not, however, form a hydrochloride in the usual way, and all attempts to obtain a second isomeride have been unsuccessful.

In no case has a substituted benzaldoxime containing a hydroxyl group in the nucleus been obtained in two forms, although *p*-acetoxybenzaldoxime and anisaldoxime both give a *syn*-compound. It was thought that substituted hydroxybenzaldoximes, particularly those containing a heavy group in the ortho-position with respect to the hydroxyl group, might exist in two forms, as the entrance of other groups might exert a "steric hindrance" effect. 5-Bromovanillinoxime and 5-nitrovanillinoxime have already been investigated, with negative results (Brady and Dunn, T., 1915, 107, 1858), and 3:5-dibromo-*p*-hydroxybenzaldoxime and 3:5-dibromo-*o*-hydroxybenzaldoxime have now been studied. The former yields a hydrochloride in the usual way, but this regenerates the original oxime on decomposition with sodium carbonate solution; the latter does not form a hydrochloride, and cannot therefore be converted into an isomeride.

Although anisaldoxime readily gives a *syn*-derivative, *o*-methoxybenzaldoxime and 3:4-dimethoxybenzaldoxime (veratraldoxime) exist only in the *anti*-form. The influence of the introduction of the bromine atom into these compounds has been investigated, and, whilst it has been found that 5-bromo-*o*-methoxybenzaldoxime cannot be converted into a *syn*-isomeride through the hydrochloride, 5-bromo-3:4-dimethoxybenzaldoxime, on the other hand, yields an unusually stable *syn*-derivative, remarkable in that its acetyl derivative is not decomposed to the nitrile by sodium carbonate solution, but only by sodium hydroxide solution.

These results have not made less puzzling the failure to obtain *syn*-isomerides from some substituted benzaldoximes.

It is evident that the introduction of negative substituents is not a determining factor, and the inhibitive effect of the hydroxyl group on the formation of *syn*-isomerides has been further demonstrated. Two more benzaldoximes, which do not give hydrochlorides when treated in dry ethereal solution with dry hydrogen chloride, have been added to the previously unique case of 6-nitropiperonaloxime.

#### EXPERIMENTAL.

*Attempted Conversion of 2:4-Dinitrobenzaldoxime.*—The oxime, prepared from the aldehyde, hydroxylamine hydrochloride, and sodium carbonate in alcohol, was dissolved in dry ether and the solution saturated with dry hydrogen chloride. No hydrochloride was precipitated, and evaporation of the ethereal solution in a current of dry air gave the unchanged oxime. An attempt was

made to bring about the conversion by Dunstan and Thole's method (P., 1911, 27, 233), but without success. Ciamician and Silber (Ber., 1903, 36, 4268) found that the nitrobenzantialdoximes, when exposed to sunlight in benzene solution in sealed tubes, were converted into the nitrobenzsynaldoximes. Similar experiments are being tried with 2:4-dinitrobenzaldoxime and other oximes; the results will be described in a subsequent communication.

*Acetyl Derivative.*—The configuration of the oxime was determined by the preparation of its acetyl derivative, and the subsequent hydrolysis of this compound to the oxime. The oxime was treated with about four times its weight of acetic anhydride and warmed to 30°. The oxime dissolved, and, on decomposing the excess of acetic anhydride with sodium carbonate solution, the acetyl derivative separated; from dilute alcohol it forms yellow, microscopic crystals melting at 79° (Found: Ac=17.4.  $C_9H_7O_6N_3$  requires Ac=17.0 per cent.).

On warming with 10 per cent. sodium hydroxide solution for some minutes, the acetyl compound dissolved, and, on addition of dilute sulphuric acid, the original oxime was precipitated. The *anti*-configuration of 2:4-dinitrobenzaldoxime is thus established.

*3:5-Dibromo-p-hydroxybenzaldoxime.*—To 28 grams of 3:5-dibromo-p-hydroxybenzaldehyde, prepared by Paal's method (Ber., 1895, 28, 2408), were added 100 c.c. of 10 per cent. sodium hydroxide solution; the aldehyde dissolved, and the sodium salt crystallised out almost immediately. A further 200 c.c. of water was added, together with 8 grams of hydroxylamine hydrochloride in water, and the mixture was left overnight. At the end of that time the precipitated sodium salt of the aldehyde had completely disappeared, and, on acidifying the solution with dilute sulphuric acid, the oxime was precipitated. It crystallises from alcohol in colourless needles melting at 199° (Paal and Kromschröder, Ber., 1895, 28, 3236, give 194°) (Found: Br=53.9. Calc.: Br=54.2 per cent.).

The hydrochloride, prepared by saturating a solution of the oxime in dry ether with dry hydrogen chloride, was precipitated as a white, crystalline powder melting and decomposing at 190° (Found: Cl=10.3.  $C_7H_5O_2NBr_2HCl$  requires Cl=10.7 per cent.). The hydrochloride was decomposed with sodium carbonate solution and the oxime precipitated with dilute sulphuric acid; this was found to be the unaltered *anti*-derivative.

*The Diacetyl Derivative.*—The oxime is not acetylated with the ease that is usually observed, and one drop of concentrated sulphuric acid is needed as a catalyst. The oxime was covered with acetic anhydride and the sulphuric acid added; the compound

dissolved rapidly, and the liquid became just appreciably warm. Excess of acetic anhydride was removed with sodium carbonate, and the acetyl derivative separated as a gum-like material. This substance was difficult to crystallise, but when dissolved in the minimum amount of boiling absolute alcohol, and the liquid cooled and the walls of the vessel scratched for some minutes, it separated as a white, crystalline powder melting at 122° (Found: Ac=22.8.  $C_{11}H_9O_4NBr_2$  requires Ac=22.7 per cent.). When heated for fifteen minutes with 10 per cent. sodium hydroxide, the diacetyl compound regenerates the original oxime, thus establishing the *anti*-configuration of that substance.

*3:5-Dibromo-*o*-hydroxybenzaldoxime.*—The preparation of 3:5-dibromo-*o*-hydroxybenzaldoxime has been described by Heerlein (*Berz. Jahrest.*, 25, 486) and Werner (*Bull. Soc. chim.*, 1886, [ii], 46, 277), but a more satisfactory method consists in dissolving salicylaldehyde in glacial acetic acid and adding the calculated quantity of bromine in acetic acid, the mixture being kept cool. After remaining for some time, the addition of water precipitates the aldehyde, which may be crystallised from alcohol. To a solution of 16 grams of the aldehyde in alcohol, 5 grams of hydroxylamine hydrochloride dissolved in a minimum quantity of water were added, followed by 5 grams of sodium hydroxide in concentrated aqueous solution. The mixture was allowed to remain overnight, the oxime precipitated by the addition of excess of dilute sulphuric acid, and crystallised first from alcohol and then from benzene. *3:5-Dibromo-*o*-hydroxybenzaldoxime* separates from benzene in colourless needles melting at 204° (Found: Br=54.2.  $C_9H_9O_2NBr_2$  requires Br=54.2 per cent.).

The diacetyl derivative, prepared in the usual way, crystallises from alcohol in colourless needles melting at 111.5° (Found: Ac=22.4.  $C_{11}H_9O_4NBr_2$  requires Ac=22.7 per cent.). On hydrolysis with 10 per cent. sodium hydroxide, the diacetyl compound regenerated the original oxime, which is accordingly the *anti*-isomeride.

*5-Bromo-*o*-methoxybenzaldoxime.*—*5-Bromo-*o*-methoxybenzaldoxime* was prepared by Perkin (*Annalen*, 1868, 145, 304) by the bromination of *o*-methoxybenzaldehyde; it may, however, be more economically prepared from 5-bromosalicylaldehyde, obtained by the bromination of salicylaldehyde (Piria, *Annalen*, 1839, 30, 71). Twenty grams of 5-bromosalicylaldehyde were dissolved in a solution of 8 grams of sodium hydroxide in 200 c.c. of water, and 4 grams of methyl sulphate added with constant shaking. The methyl ether separated as a solid, and, after some time, was collected and crystallised from alcohol. Ten grams of the aldehyde

were dissolved in 50 c.c. of alcohol, and 4 grams of hydroxylamine hydrochloride and 4 grams of sodium hydroxide, each dissolved in the minimum quantity of water, were added. After remaining overnight, the oxime was precipitated by acidifying with dilute sulphuric acid, and crystallised from methyl alcohol, from which it separated in long, colourless needles melting at 109° (Found: Br=34.5.  $C_8H_8O_2NBr$  requires Br=34.8 per cent.).

The *acetyl* derivative crystallises from alcohol in colourless prisms melting at 102° (Found: Ac=15.3.  $C_{10}H_{10}O_3NBr$  requires Ac=15.8 per cent.). Hydrolysis of this compound to the original oxime with sodium hydroxide solution established the *anti*-configuration of the latter.

*Hydrochloride of 5-Bromo-*o*-methoxybenzaldoxime.*—The oxime was dissolved in dry ether and the solution saturated with dry hydrogen chloride. The hydrochloride was precipitated as a yellow, crystalline powder melting and decomposing at 123° (Found: Cl=13.1.  $C_8H_8O_2NBr, HCl$  requires Cl=13.3 per cent.). The hydrochloride, on decomposition with sodium carbonate solution, gave a crude oxime melting at 100°. Part was recrystallised from acetone and water, when it gave a compound, which was proved to be the original oxime by the method of mixed melting points. The rest was treated with acetic anhydride, and gave the *acetyl* derivative, which, on hydrolysis, gave the original oxime. Accordingly, no conversion to the *syn*-isomeride had taken place.

*5-Bromo-3:4-dimethoxybenzaldoxime.*—Eighteen grams of 5-bromoveratraldehyde, prepared from 5-bromovanillin by methylation with methyl sulphate (Dakin, *Amer. Chem. J.*, 1909, **42**, 494), were dissolved in 50 c.c. of alcohol, and 6 grams of hydroxylamine hydrochloride and 3 grams of sodium hydroxide, each in the minimum amount of water, were added. After remaining overnight, the oxime was precipitated by the addition of dilute sulphuric acid and recrystallised from dilute alcohol, when it separated in colourless, shining needles melting at 83° (Found: Br=30.4.  $C_9H_{10}O_3NBr$  requires Br=30.8 per cent.).

The *acetyl* derivative was prepared in the usual way, and its hydrolysis confirmed the *anti*-configuration of the original oxime. It crystallises with difficulty from dilute methyl alcohol in microscopic crystals melting at 77° (Found: Ao=14.3.  $C_{11}H_{12}O_3NBr$  requires Ac=14.2 per cent.).

*Hydrochloride of 5-Bromo-3:4-dimethoxybenzaldoxime.*—The *anti*-oxime was dissolved in dry ether and the solution saturated with dry hydrogen chloride, when the hydrochloride was precipitated as a white, crystalline powder melting and decomposing at 120—125° (Found: Cl=11.8.  $C_9H_{10}O_3NBr, HCl$  requires Cl=12.0 per cent.).

*5-Bromo-3:4-dimethoxybenzaloxime.*—The above hydrochloride was decomposed with sodium carbonate solution, and the crude oxime melted at 108°. Crystallisation from acetone and water gave the pure *syn*-oxime in small prisms melting at 116° (Found: Br=30.9.  $C_9H_{10}O_3NBr$  requires Br=30.8 per cent.).

*Acetyl Derivative.*—The *syn*-oxime was treated with about four times its weight of acetic anhydride, the solution warmed to 30°, and the excess of acetic anhydride decomposed with sodium carbonate solution. Unlike the acetyl derivatives of other *syn*-oximes that have been studied, that derived from 5-bromo-3:4-dimethoxybenzaloxime is not decomposed in these circumstances with the formation of nitrile, and the solid which separated proved to be the acetyl derivative. When crystallised from dilute alcohol, it tended to separate as an oil, which slowly solidified, but after two recrystallisations it melted sharply at 73° (Found: Ac=13.9.  $C_{11}H_{12}O_4NBr$  requires Ac=14.2 per cent.).

The *acetyl* derivative was warmed with 10 per cent. sodium hydroxide solution to 35°. After cooling and diluting, the solid was crystallised from alcohol, and found to be 5-bromoveratronic nitrile (m. p. 117°), giving, on boiling with sodium hydroxide, ammonia and 5-bromoveratric acid.

*5-Bromoveratronic nitrile.*—For the purpose of identification of the product obtained by treating the above acetyl compound with sodium hydroxide, the nitrile was prepared by boiling 5-bromo-3:4-dimethoxybenzaloxime with excess of acetic anhydride for three hours. The excess of anhydride was decomposed with sodium carbonate solution, and the solid was crystallised from alcohol, when the nitrile separated in colourless, microscopic crystals melting at 117° (Found: Br=32.8.  $C_9H_8O_2NBr$  requires Br=33.1 per cent.).

The nitrile, on boiling for thirty minutes with 10 per cent. sodium hydroxide solution, is completely hydrolysed, and, on acidifying the solution, 5-bromoveratric acid (m. p. 189°) is precipitated. Zincke and Francke (*Annalen*, 1896, 293, 183), who obtained this acid from methyl 5-bromoprotocatechuate by methylation and subsequent hydrolysis, give 191° as the melting point, and Pechorr (*Annalen*, 1912, 391, 31), who obtained it by the oxidation of 5-bromoveratraldehyde, gives 192–193°.

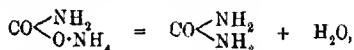
The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this research.

ORGANIC CHEMICAL LABORATORIES,  
UNIVERSITY COLLEGE, LONDON. [Received, August 4th, 1920.]

CXVII.—*The Constitution of Carbamides. Part XI. The Mechanism of the Synthesis of Urea from Ammonium Carbamate. The Preparation of certain Mixed Tri-substituted Carbamates and Dithiocarbamates.*

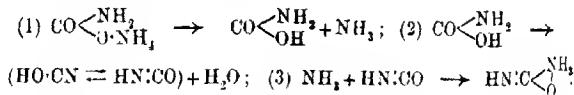
By EMIL ALPHONSE WERNER.

IN 1868 Basarov (*J. pr. Chem.*, [ii], 1, 283; *Journ. Chem. Soc.*, 21, 194) obtained urea by the action of heat on ammonium carbamate under pressure. The change, which is supposed to be obviously explained by the simple equation



is always considered to represent the converse of the ultimate hydrolysis of urea to ammonium carbonate, and for this reason this synthesis is commonly cited as evidence *par excellence* in favour of the deceptive "carbamide" configuration.\*

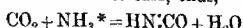
To satisfy this view, it has been assumed, without any proof, that water is eliminated from the group  $\cdot\text{O} \cdot \text{NH}_4$ , the production of urea being thus analogous to the formation of acetamide from ammonium acetate, or of oxamide from ammonium oxalate. As a matter of fact, the mechanism of the formation of urea in this reaction is of quite a different order, since it is nothing more than a modification of Wöhler's synthesis, namely, the production of urea from ammonia and cyanic acid ( $\text{HN:CO}$ ) as the result of the following series of changes:



So far as ammonium carbamate is concerned, the fact that urea and ammonium cyanate were found in the product after vaporising the salt through a glass tube heated to incipient redness is not final proof that cyanic acid was produced as shown above, since Mixter (*Amer. Chem. J.*, 1882, 4, 35) obtained urea from carbon

\* It may be of interest to record that Kolbe, in presenting Basarov's paper to the Society, opens with the words: "From the conviction that urea is not carbamide"—a remark which, the author is equally convinced, has been fully justified.

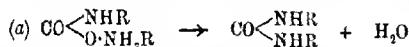
dioxide and ammonia at a red heat. There can be no doubt that cyanic acid was generated in this case, thus,



(see Expt. VI), as Mixter suggested.

Convincing evidence, however, in support of the above series of changes has been obtained from a study of the decomposition of certain substituted ammonium carbamates and dithiocarbamates.

Fichter and Becker (*Ber.*, 1911, **44**, 3473, 3481) showed that methylammonium methylcarbamate,  $\text{NHMe} \cdot \text{CO} \cdot \text{O} \cdot \text{NH}_3\text{Me}$ , and the ethylammonium analogue gave the respective symmetrical disubstituted carbamides, whilst no tetra-substituted carbamide could be obtained from diethylammonium diethylcarbamate. Since direct dehydration of the carbamates was assumed to represent the mechanism of the change, it follows that if the reaction

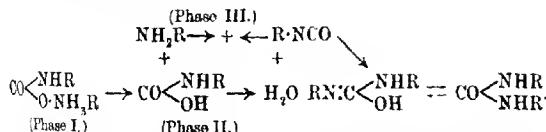


was the result of the direct elimination of water from the group  $\cdot \text{O} \cdot \text{NH}_3\text{R}$ , there seemed no reason why the change



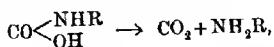
should not take place with even greater facility than in the case of reaction (a). Since loss of water could take place in one way only, and considering the stability of tetra-substituted carbamides, these investigators were unable to explain the apparent abnormality.

Now, according to the three-phase change, or "dissociation theory" here put forward, only carbamates which contain the system  $\text{CO} \cdot \text{NHR}$ , capable of yielding  $\text{R} \cdot \text{NCO}$ , can give rise to substituted carbamides. Thus, in the decomposition of all such carbamates, change (a), for example, is correctly represented by the following general scheme:

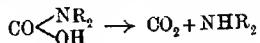


\* This reaction may prove to be of considerable importance in the near future as a method for the fixation of nitrogen as urea, since it very probably only awaits the discovery of a suitable catalyst to realise the change on an economic scale. Of great interest, in this connexion, is the recent discovery by Mailhe (*Ann. Chim.*, 1920, [ix], 13, 226) that the change  $\text{CO} + \text{NH}_3 = \text{HCN} + \text{H}_2\text{O}$  is quantitative at  $430-450^\circ$  in the presence of thorium oxide.

Whilst under normal pressure carbamio acid and its mono-substituted homologues are decomposed, thus,



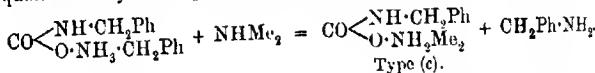
this change must be largely suppressed under high pressure in favour of the alternative one represented by phase II. In the case of a disubstituted carbamic acid, the change



alone prevails, and hence a tetra-substituted carbamide is not formed.

The soundness of the present theory has been experimentally tested by proving, as predicted by the scheme, that carbamates of type (c),  $\text{CO} \begin{cases} \text{NHR} \\ \text{O-NH}_2\text{R}' \end{cases}$ , yielded tri-substituted carbamides (as the result of phase III,  $\text{RNCO} + \text{NHR}_2 = \text{CO} \begin{cases} \text{NR}_2 \\ \text{NHR}' \end{cases}$ ), whilst those of type (d),  $\text{CO} \begin{cases} \text{NR}, \\ \text{O-NH}_2\text{R}' \end{cases}$ , did not. Carbamates of the latter types, which have not been hitherto described, were successfully prepared by a method based on the differences in the relative strengths of the amines, to which the author has recently drawn attention (T., 1918, 113, 899; 1919, 115, 1012).

Benzylammonium benzylcarbamate in cold alcoholic solution was quantitatively decomposed by dimethylamine, thus:



*Dimethylammonium benzylcarbamate* gave, after four hours at 140—150° in a sealed tube, *benzyldimethylcarbamide*,



*Diethylammonium benzylcarbamate* gave, under like conditions, *benzyldiethylcarbamide*.

*Methylammonium diethylcarbamate*,  $\text{NH}_3\text{Me}\text{-O-CO-NET}_2$  (type d), was prepared by the displacement of diethylamine from diethylammonium diethylcarbamate by the stronger amine, methylamine. After four hours at 145—150°, it failed to yield any methyl-diethylcarbamide (Expt. V).

It is obvious that the theory of the direct dehydration of carbamates, which fails entirely to explain the facts just recorded, must be abandoned in favour of the dissociation theory. As a logical sequence thereof, Basarov's synthesis of urea can no longer be upheld as evidence of the "carbamide" structure.

*The Decomposition of Dithiocarbamates.*

It is well known that dithiocarbamates derived from the interaction of carbon disulphide and primary amines, namely,  $RHN\cdot CS\cdot S\cdot NH_2R$  (type *e*), yield symmetrical disubstituted thiocarbamides, whilst those derived from secondary amines, namely,  $R_2N\cdot CS\cdot S\cdot NH_2R_2$  (type *f*), do not yield tetra-substituted thiocarbamides.

A study of the decomposition of the following "mixed" dithiocarbamates, of types which have not been hitherto prepared, has proved that the mechanism of the changes is similar to that of carbamates.

*Dimethylammonium benzylidithiocarbamate,*



prepared from benzylammonium benzylidithiocarbamate by the displacement of benzylamine by dimethylamine (Expt. III), gave *benzyldimethylthiocarbamate*,  $NMe_2\cdot CS\cdot NH\cdot CH_2Ph$ , after an alcoholic solution was boiled under reflux until hydrogen sulphide ceased to be evolved.

*Diethylammonium benzylidithiocarbamate,*



similarly gave *benzyldiethylthiocarbamate* (Expts. III and IV).

Since dithiocarbamates of type (*f*) which contain the system  $S\cdot NH_2R_2$  do not yield thiocarbamides, there can be no doubt that the above results were the outcome of a reaction between  $NHR_2$  and  $C_6H_5\cdot CH_2\cdot NCS$  (phase III), produced in accordance with the general scheme.

To prove that thiocarbamates of type (*g*),  $NH_3R\cdot S\cdot CS\cdot NR_2$ , did not yield tri-substituted thiocarbamides, *methylammonium dimethylidithiocarbamate* (m. p. 90–91°) and *methylammonium diethylidithiocarbamate*, large, hexagonal prisms (m. p. 103°), were prepared. In each case, methylamine and hydrogen sulphide were evolved when alcoholic solutions of the respective salts were heated to 100° under reflux. Whilst no tri-substituted thiocarbamido could be isolated from the product, the main change was a bimolecular decomposition of the acid,  $R_2N\cdot CS\cdot SH$ , produced by dissociation of the original salt, as the preliminary change. The theory that the formation of substituted thiocarbamides from dithiocarbamates is simply a direct elimination of hydrogen sulphide is therefore a fallacy.

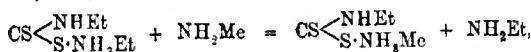
The well-known fact that ammonium dithiocarbamate,  $R_4N\cdot CS\cdot S\cdot NH_4$ , yields only ammonium thiocyanate when decomposed by heat under normal pressure is due to the change occurring

below the temperature at which an equilibrium,  $\text{HS}\cdot\text{CN} \rightleftharpoons \text{HN}\cdot\text{CS}$ , can obtain, the form  $\text{HN}\cdot\text{CS}$  being essential to the production of thiourea by its union with ammonia (T., 1912, 101, 2184; 1919, 115, 1169).

*The Preparation of "Mixed" Dithiocarbamates.*

Apart from their theoretical interest, the preparation of dithiocarbamates of types  $\text{CS} \leftarrow \begin{smallmatrix} \text{NHR} \\ \text{S} \cdot \text{NH}_2 \text{R}_2 \end{smallmatrix}$  and  $\text{CS} \leftarrow \begin{smallmatrix} \text{NHR} \\ \text{S} \cdot \text{NH}_2 \text{R} \end{smallmatrix}$  is of some practical importance, since it provides a simple means for obtaining various mixed di- and tri-substituted thiocarbamides by dispensing with the preparation of the otherwise necessary thiocarbimide,  $\text{R}\cdot\text{NCS}$ .

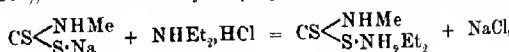
The "displacement" method is not recommended when there is only a small difference between the relative strengths of the amines; thus, in order to realise the reaction,



it was necessary to use a considerable excess of methylamine (3–4 molecules) to complete the change within a reasonable time. On the other hand, *n*-butylamine, for example, was readily displaced from *n*-butylammonium *n*-butyldithiocarbamate,  $\text{C}_9\text{H}_{22}\text{N}_2\text{S}_2$ , by dimethylamine, with the production of dimethylammonium *n*-butyldithiocarbamate,  $\text{C}_7\text{H}_{18}\text{N}_2\text{S}_2$  (refractive hexagonal prisms, m. p. 93.5°).

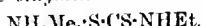
With closely related amines, admirable results were obtained by dissolving the amine hydrochloride in either an aqueous or alcoholic solution of the sodium salt of the particular dithiocarbamic acid, prepared according to the method described by Delépine (*Compt. rend.*, 1907, 144, 1126).

*Diethylammonium methylidithiocarbamate* (prisms, m. p. 89–90°), which could only be prepared according to the equation



gave methylidethyldithiocarbamide in a yield equal to 72 per cent. of the theoretical.

*Dimethylammonium ethyldithiocarbamate*,



(m. p. 101°), from sodium ethyldithiocarbamate and dimethylammonium chloride, gave a yield of dimethylethyldithiocarbamide equal to 67 per cent. of the theoretical.

## EXPERIMENTAL.

*Preparation of Mixed Benzylcarbamates and Benzyl Dithiocarbamates.*

*Expt. I.*—Thirteen grams of benzylammonium benzylcarbamate (m. p. 101°), prepared by passing carbon dioxide through a solution of benzylamine in dry ether, were placed in a stout tube of soft glass, and 3·5 grams of dimethylamine dissolved in 20 c.c. of alcohol were added. A clear solution was obtained after the mixture had remained at the ordinary temperature for twenty-four hours, when 40 c.c. of ether were added. The viscous *dimethylammonium benzylcarbamate* was allowed to subside, after which the mixture of ether and alcohol, which contained free benzylamine, was poured off. The product was twice treated with 15 c.c. of ether to remove all free amines (Found, by hydrolysis with ammoniacal calcium chloride and titrating the calcium carbonate with hydrochloric acid:  $\text{CO}_2$ =21·73.  $\text{C}_{10}\text{H}_{16}\text{O}_2\text{N}_2$  requires  $\text{CO}_2$ =22·44 per cent.). The tube was sealed, and, after heating at 140° for four hours, the semi-solid product was extracted with water. The insoluble *benzyldimethylcarbamide* (2·6 grams) crystallised from alcohol in colourless, glistening needles, which melted at 166° (Found: N=15·81.  $\text{C}_{10}\text{H}_{14}\text{ON}_2$  requires N=15·73 per cent.). The yield was equal to 29·2 per cent. of the theoretical. A specimen prepared from benzyl cyanate and dimethylamine had the same melting point and a similar appearance.

*Expt. II.*—This was a repetition of I with diethylamine in place of the methyl compound. From *diethylammonium benzylcarbamate*, a viscous liquid, 3·7 grams of *benzyldiethylcarbamide*, slender, glistening prisms melting at 169–170°, in a yield equal to 36 per cent. of the theoretical, were isolated (Found: N=13·66.  $\text{C}_{12}\text{H}_{18}\text{ON}_2$  requires N=13·59 per cent.).

*Expt. III.*—Carbon disulphide (3·8 grams) was added to benzylamine (10·7 grams) in 25 c.c. of alcohol. To the benzylammonium benzylthiocarbamate formed, dimethylamine (4·7 grams) in 10 c.c. of alcohol was added. After twenty-four hours, 9 grams of *dimethylammonium benzylthiocarbamate*, brilliant, small, rhomboidal prisms, were collected (m. p. 116–117°) (Found: S=28·19.  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{S}_2$  requires S=28·07 per cent.).

Five grams of the salt, in 30 c.c. of alcohol, were boiled under reflux until evolution of hydrogen sulphide had ceased. On adding water, *benzyldimethylthiocarbamide* was precipitated in slender, rhombic prisms melting at 95–96°. The yield (3·2 grams) was equal to 75·3 per cent. of the theoretical (Found: S=16·39; N=14·55.  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}$  requires S=16·49; N=14·43 per cent.).

*Expt. IV.*—When diethylamine (5·4 grams) replaced dimethylamine in the previous experiment, 9·7 grams of *diethylammonium benzylidithiocarbamate*, stout, hexagonal prisms melting at 111°, were obtained (Found: S=25·17.  $C_{12}H_{20}N_2S_2$  requires S=25·0 per cent.). Five grams gave *benzyldiethylthiocarbamide* (3·42 grams), silky needles melting at 67°, in a yield equal to 79 per cent. of the theoretical (Found: S=14·29.  $C_{12}H_{18}N_2S$  requires S=14·41 per cent.).

*Methylammonium Diethylcarbamate.*

*Expt. V.*—Diethylammonium diethylcarbamate (10 grams), prepared by the union of carbon dioxide and the vapour of pure diethylamine, as recommended by Fichter and Becker (*loc. cit.*), was allowed to remain for twenty-four hours in contact with a solution of methylamine (6 grams) in a mixture of ether and alcohol contained in a separating funnel. The viscous liquid was subjected to a second treatment with methylamine (3 grams), after which it was well extracted with pure ether to remove all free amine. It gave no precipitate with a solution of calcium chloride in the cold, but a copious precipitate of calcium carbonate when warmed [Found:  $CO_2$  (on hydrolysis)=29·06.  $C_6H_{16}O_2N_2$  requires  $CO_2$ =29·72 per cent.]. The original ethyl compound requires  $CO_2$ =23·15 per cent., hence the displacement of the diethylammonium group was practically complete. Five grams heated for four hours in a sealed tube at 140–150° gave a product which volatilised completely at 100°. No methyl-diethylcarbamide, therefore, was formed.

*Formation of Urea and Ammonium Cyanate from Ammonium Carbamate.*

*Expt. VI.*—Ammonium carbamate, contained in a flask attached to a tube of hard glass (120 cm. long and 1·5 cm. bore), was vaporised in a current of dry ammonia, while the tube was maintained at a low red heat over a length of 80 cm., the forward portion being cooled by a circulating current of water. The presence of ammonium cyanate in the sublimate, which was collected, was proved by the formation of a precipitate of silver cyanate in a solution of the product carefully neutralised by nitric acid to which silver nitrate had been previously added to avoid the loss of cyanic acid by hydrolysis. Urea was detected by the xanth-hydroxyl reaction and by the formation of its nitrate.

Whilst this experiment may be considered a repetition of

Mixter's (*loc. cit.*), the presence of ammonium cyanate, which was not pointed out by this investigator, is of much theoretical interest, since, in the author's opinion, it is formed side by side with urea, and not necessarily from the latter, generated beforehand.

*Summary.*

- (1) The formation of urea from ammonium carbamate is no evidence of the "carbamide" structure, since it arises from the interaction of ammonia and cyanic acid ( $\text{HN}\cdot\text{CO}$ ), as in Wöhler's synthesis.
- (2) A scheme which explains the formation of substituted ureas and thioureas from substituted carbamates and thiocarbamates, and is in agreement with all the known facts, has been experimentally proven.
- (3) Methods for the preparation of "mixed" dithiocarbamates are described, from which corresponding di- and tri-substituted thioureas may be conveniently obtained.

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[*Received, July 27th, 1920.*]

XVIII.—*A Comparative Study in the Xanthone Series. Part I.*

By SURENDRA NATH DHAR.

In the series of investigations of which this is Part I, it is intended to compare xanthone with other compounds having similarities in structure or properties. In the first place, such a comparison is attempted with anthraquinone, which has the greatest similarity to xanthone. No comparative study seems to have been made systematically by anyone except Hertzig (*Monatsh.*, 1891, **12**, 161), who found that enxanthone is more stable than quercetin (a flavone), and Graebe and Eichengrün (*Ber.*, 1891, **24**, 967), who compared some hydroxyxanthones with certain hydroxyanthraquinones and hydroxybenzophenones. Other attempts at a comparison of xanthone with anthraquinone with respect to the colouring properties of their hydroxy-derivatives are evidenced from a few isolated instances. Thus Graebe and Aders (*Annalen*, 1901, **318**, 365) showed the similarity of the hydroxyl group in position 1 in both the series. A. G. Perkin and Everest

have incidentally raised the same question ("The Natural Organic Colouring Matters," pp. 126—127). They compare alizarin with 3:4-dihydroxyxanthone, but, as a matter of fact, 1:2-dihydroxyxanthone, and not the 3:4-derivative, corresponds with alizarin. Attempts are being made to synthesise 1:2-dihydroxyxanthone, and the results will be communicated in due course. At the same time, a systematic comparison is being attempted in the following directions: (1) nitration; (2) direct displacement of nitro-groups by halogens, methoxy-group, etc., and certain other important reactions with nitro-compounds, such as Skraup's synthesis, Doebner and Miller's and Knorr's syntheses, etc.; (3) halogenation; (4) mobility of halogen atoms; (5) migration of diazo-groups.

It is interesting to note that xanthone has been found to be much more reactive than anthraquinone. Thus with nitric acid alone, xanthone gives two dinitroxanthones ( $\alpha$  and  $\beta$ ), whereas anthraquinone gives a mononitro-derivative only (*Ber.*, 1883, 16, 363). Again, quite a number of tri- and tetra-nitroxanthones have very easily been prepared, whilst no such polynitro-derivatives of anthraquinone are known, and further nitration of the dinitro-compounds has not yet been effected.

Xanthone seems not only to be more reactive, but also more stable, although from the structure of these compounds such a fact is quite unexpected. It is well known that when fused with potassium hydroxide, xanthone decomposes into 1:1'-dihydroxybenzophenone, whereas anthraquinone is completely degraded to two molecules of benzoic acid. Similarly, it has been found that when further nitration of 1:5- or 1:8-dinitroanthraquinone is attempted with mixtures of nitric and sulphuric acids, they decompose completely, whilst both  $\alpha$ - and  $\beta$ -dinitroxanthones are converted into tetrinitroxanthones at an earlier stage of such a treatment, and the products are not decomposed on subsequent treatment. It may also be noted that tetrabromoxanthone is nitrated and not decomposed by such a mixturo (Dhar, *T.*, 1916, 109, 740).

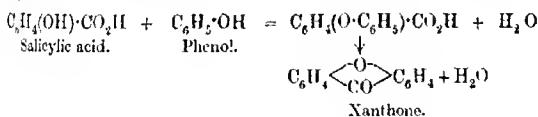
So far as the behaviour of nitroxanthone has been studied, it has been found that the nitro-groups in the xanthone series are much more readily displaced by direct bromination than is the case in the anthraquinone series (see this vol., p. 994).

Skraup's synthesis is effected much more readily in the xanthone series than in the anthraquinone series, and xanthone has also been found to be much more reactive towards halogens than anthraquinone. Thus two hexabromo- and an octabromoxanthone have been prepared, whereas no such corresponding

bromo-compounds are known in the anthraquinone series. When treated with bromine in sealed tubes, xanthone gives the 2:7-dibromo-derivative (Graebe, *Annalen*, 1889, **254**, 284), whilst anthraquinone gives 1:2-dibromoanthraquinone.

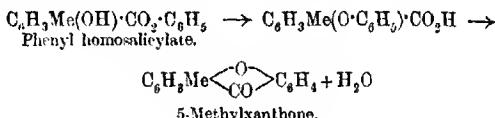
### Theory of the Formation of Xanthone.

Strohbach has discussed in detail the various theories put forward to explain the formation of xanthone (*Ber.*, 1901, **34**, 4136). He attacked mainly the theories of Graebe and Seifert, and, after proving them incapable of explaining all the experimental facts then known, he tried to establish a new theory of his own, together with a few empirical rules. One thing is, however, common to all the theories, and that is the supposition that phenol does not take part in the formation of xanthone or its derivatives. On the other hand, if phenol is supposed to take part in the reaction, the formation of xanthone becomes very simple and does not necessitate the supposition of various intermediate products, the existence of which is doubtful, or any transposition of groups which Strohbach was compelled to make. Thus, in order to ascertain whether phenol takes part or not, experiments were made on the preparation of xanthone from salicylic acid, using in each case an equimolecular proportion of phenol. It is remarkable that the yield of xanthone in each case was just double when phenol was employed. That phenol actively takes part in the reaction and raises the yield in such a remarkable and systematic way is proved beyond doubt by the facts that when nitrobenzene is used instead of phenol, no increase in the yield of xanthone is effected, and when *o*-nitrophenol is used, 4-nitroxanthone is obtained. The formation of xanthone may therefore be explained thus:



When only salicylic acid is used, half is decomposed into phenol, and traces of phenol can actually be detected in such experiments. The use of a dehydrating agent increases the yield by removing the water formed in the reaction. When acetic anhydride is used, the first reaction is most probably the acetylation of the phenolic group, and this seems to be an important factor in the yield. That is why *o*-acetoxybenzoic acid gives xanthone, and the yield is not affected in the least whether acetic anhydride is used or not.

Now the formation of xanthone from phenyl salicylate, as well as all the other typical instances cited by Strohbach, may be explained by this theory; and the yield is necessarily poor when neither the phenolic groups are acetylated nor any dehydrating agent is used. Thus the formation of xanthone from phenyl salicylate proceeds according to Graebe's first two equations (*loc. cit.*), and the liberated salicylic acid and phenol are not wasted, as he has supposed, but give xanthone again, although the yield in such a case is quite inappreciable, as will be shown in the experimental part (p. 1061). The formation of 5-methyl- and 4:5-dimethyl-xanthone from phenyl homosalicylate supplies another instance in support of this theory. Thus:



The water formed here hydrolyses one molecule of the ester, giving phenol and homosalicylic acid, which may give a further amount of the same methylxanthone, but the main reaction takes the following course. One of a pair of homosalicylic acid molecules gives *o*- cresol, just as salicylic acid gives phenol, and the condensation takes place in the usual way, giving 4:5-dimethylxanthone. It is interesting to note that, according to Graebe's theory, only 5-methylxanthone, and according to Strohbach's theory, only 4:5-dimethylxanthone, is possible, and according to Seifert's theory none of these is possible, whereas, according to the present theory, both products can be formed. The other instances cited in Strohbach's paper may be explained similarly.

After elucidating the mechanism of the formation of xanthone, a few experiments were made in order to ascertain whether the change takes place gradually or suddenly, and in the case of a sudden change to find the temperature at which it takes place. The temperature of the reaction mixture was therefore recorded, particularly carefully when a single substance was used. The results show conclusively that the conversion takes place gradually, as there was no sudden change in the temperature. Attempts have also been made to synthesise xanthone by various other methods, and it has been found that the condensation of *o*-chlorobenzoic acid with phenol (Ullmann's method) gives most satisfactory results, the yield of xanthone being almost theoretical and the process very simple.

*o*-Thiolbenzoic acid condenses with benzene and its simple deriv-

atives in the presence of sulphuric acid, giving thioxanthone and its derivatives (*Annalen*, 1896, **149**, 250), but salicylic acid does not condense with benzene or its derivatives either under these conditions or under the influence of phosphoryl chloride or with acetic anhydride in sealed tubes.

*Fluorescence of Xanthone and its Derivatives.*

The fluorescence of the two nitroxanthones (2- and 3-) is rather unexpected, as it is generally found that the introduction of a nitro-group destroys the fluorescence (Ullmann, *Annalen*, 1907, **355**, 312). Still more striking is the fact that the colour of the fluorescence is deeper in the case of the nitro-compounds. Thus xanthone shows only blue fluorescence, whereas 2- and 3-nitroxanthone show greenish-blue and green fluorescence respectively. Very few di-derivatives of a fluorescent substance are found to be fluorescent, and of all the di-derivatives described in this paper, only dichloroxanthone is fluorescent.

*Nitroxanthones.*

Only four nitro-derivatives of xanthone have been described. One (3-nitroxanthone) was prepared by Ullmann by condensing 2-chloro-4-nitrobenzoic acid with phenol (*Annalen*, 1904, **355**, 341), and 2:4-dinitroxanthone was prepared by Mayer (*Ber.*, 1909, **42**, 1132) by a similar method. The other two ( $\alpha$ - and  $\beta$ -dinitroxanthones) were prepared by Perkin (*T.*, 1883, **43**, 1870) by the direct nitration of xanthone with nitric and sulphuric acids. By a slight modification of this method, these compounds were obtained in a purer condition (*T.*, 1916, **109**, 746), but it has now been found that they can be prepared from xanthone by treating it with nitric acid alone. As has been stated, xanthone differs from anthraquinone in its remarkable capacity for yielding nitro-derivatives, and the number of these has been increased from four to fifteen, and it is expected that many more can be prepared without difficulty. Two methods have mainly been employed, namely, nitration and synthesis by Ullmann's method (*loc. cit.*).

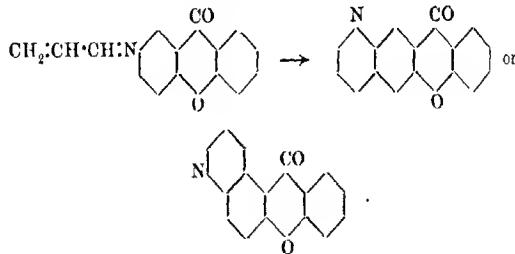
3-Nitroxanthone, which had previously been obtained only by synthesis, has now been prepared by the careful nitration of xanthone. The other three isomeric mononitroxanthones have been obtained by synthesis. *4-Nitroxanthone* is formed when salicylic acid and *o*-nitrophenol are heated with acetic anhydride, but it has not been possible to obtain this compound by the condensation of *o*-chlorobenzoic acid with *o*-nitrophenol. The remarkable fact has been observed that nitroxanthones are much more

easily nitrated than xanthone itself under the same conditions. Whereas xanthone gives only dinitroxanthones, 1- and 4-nitroxanthone give tetranitroxanthones, and 2- and 3-nitroxanthone give trinitroxanthones. As many as six tetranitroxanthones have been prepared from lower nitroxanthones with very great ease. The orientation of these tetranitro-compounds is still under investigation, but they have been distinguished from each other mainly by their bromination products. By this method it has been found that the  $\alpha_1$ - and  $\beta_1$ -tetranitro-compounds are identical, and two of their nitro-groups are so stable that they are not removed by bromine, even when heated at 300° for twenty-six hours (this vol., p. 995).

Further nitration of some of these tetranitroxanthones ( $\alpha_1$ ,  $\alpha_2$ , and  $\beta_2$ ) has been attempted by boiling them with mixtures of sulphuric acid and fuming nitric acid in various proportions, but without success.

#### *A New Heterocyclic Type.*

Skraup's reaction was utilised by F. Mayer (*Ber.*, 1909, 42, 3064) in order to fuse a pyridine ring on to a thioxanthone nucleus. He obtained thereby one thioxanthoquinoline from 2-aminothioxanthone, but he neither studied this compound thoroughly nor extended this reaction to any other member of the thioxanthone or xanthone series. It was therefore proposed to study this reaction, particularly in the xanthone series, with the expectation of obtaining a series of tetracyclic compounds where one pyridine ring would be united with a pyrone ring together with two benzene rings:



It will be seen that the pyrone ring is protected on both sides by benzene rings, whereas the pyridine ring is protected only on one side. Accordingly, the respective stability of these pyrone and pyridine rings can be usefully studied.

It has been found, as expected, that an aminoxanthone, when treated with glycerol and sulphuric acid, gives a heterocyclic compound exactly of the type represented above. The reaction takes place with such great readiness that it is sufficient to use the nitro- instead of the amino-derivative. This naturally simplifies the synthesis considerably, and Dey and Goswami (T., 1919, 115, 531) have noticed the same fact in similar syntheses in the coumarin series. In this way,  $\beta$ -dinitroanthrone gives *nitroanthraquinoline*. The utilisation of the other nitro-group for fusing another pyridine ring to the already existing tetracyclic nucleus, as well as the synthesis of this type of tetracyclic compounds from other nitro-derivatives of xanthone, are under investigation.

*Action of Sodium Methoxide on Nitroanthones.*

One remarkable reaction of the nitroanthraquinones is the ease with which a nitro group is displaced by a methoxy-group. All the known dinitroanthraquinones have been converted into their corresponding dimethoxy-compounds by boiling them with sodium methoxide. Although xanthone behaves like anthraquinone in many important reactions, it differs entirely in this particular case. None of the nitro-groups of  $\alpha$ - or  $\beta$ -dinitroanthrone is displaced by a methoxy-group when treated with sodium methoxide, but the corresponding nitroanthlyhydros are produced. These substances dissolve in alkali hydroxide as well as in concentrated acids with distinctive colours.

Colour in solutions of

Substance.	NaOH.	$H_2SO_4$ .	HCl.	$HNO_3$ .	$CH_3CO_2H$ .
$\alpha$ -Dinitroanthlyhydrol	Yellow	Deep yellow	Yellow	Pink	Orange-red
$\beta$ -Dinitroanthlyhydrol	"	"	Pale yellow	—	—

Although xanthlyhydrol is quickly converted into an ether, these dinitroanthlyhydrols do not undergo this reaction, perhaps because of the influence of the nitro-groups. When boiled with mild oxidising agents, they are converted into the original nitro-xanthones.

*Halogenation.*

Three different methods have been employed for the preparation of halogen derivatives of xanthone, namely: (1) direct halogenation; (2) synthesis according to Ullmann's method (*Annalen*, 1907, 355, 359), and (3) direct displacement of the nitro-group by halogen.

### *Chloroxanthones.*

2-Chloroxanthone was prepared by Ullmann (*loc. cit.*; compare Ullmann and Wagner, *Annalen*, 1910, **371**, 388) while studying the condensation of *o*-chlorobenzoic acid and its derivatives with phenol, 3-chloroxanthone was synthesised by Gomberg and Cone (*Annalen*, 1909, **370**, 142) by a similar method, and octachloroxanthone was prepared by Steiner (*Monatsh.*, 1915, **36**, 175) whilst studying the chlorination of cyclic ketones by means of antimony pentachloride. It is proposed to study the chlorination of xanthone systematically by all the three methods mentioned above, but at present attention has mainly been confined to the second method, by which all the possible isomeric monochloroxanthones have been synthesised.

*Chlorination.*—The direct chlorination of xanthone has not yet been carried out systematically, and the only method that has been tried is by dissolving xanthone in acetic acid and passing chlorine into the solution, using a trace of iodine as a catalyst. The products are 3-chloroxanthone and a *dichloroxanthone*; the latter can easily be obtained pure, but it is very difficult to remove the last traces of it from the former.

*Ullmann's Synthesis.*—Of the four possible monochloroxanthones, 2- and 3-chloroxanthone were synthesised by Ullmann and by Gomberg and Cone respectively (*loc. cit.*). The other two isomerides have now been prepared.

### *Bromoxanthones.*

*Bromination.*—When xanthone in acetic acid solution is heated with one molecule of bromine and a trace of iodine, 3-bromoxanthone is obtained (Dhar, T., 1916, **109**, 745; compare *Annalen*, 1909, **370**, 142), but when concentrated sulphuric acid is used as a solvent instead of acetic acid, the product is 2-bromoxanthone. Each of these bromo-compounds when heated with bromine passes easily into the same dibromo-derivative, and therefore when a slight excess of bromine is used in the preparation of a monobromo-compound, dibromoxanthone is always formed. This is the main product of the direct bromination of xanthone when the operation is carried on under different conditions and with different catalysts. One striking fact in connexion with the direct bromination of xanthone is that although xanthone is brominated in sulphuric acid solution by liquid bromine, it is not attacked by a mixture of potassium bromide and potassium bromate in sulphuric acid solution.

*Synthesis.*—2-Bromoxanthone has also been synthesised from *o*-chlorobenzoic acid and *p*-bromophenol, and 4-bromoxanthone has been obtained by a similar method.

*Direct Displacement of Nitro-group by Bromine.*—By this method, several bromoxanthones have been prepared. The method serves as the only means of preparing certain bromo-derivatives, and there is a remarkable economy of bromine as the whole amount of bromine enters the nucleus.

#### EXPERIMENTAL.

##### *Xanthone.*

One hundred grams of salicylic acid when boiled with 100 grams of acetic anhydride and distilled gave only 20 grams of xanthone (compare Graebe, *Annalen*, 1889, **254**, 280). The yield was not improved by an increase in the amount of acetic anhydride or by extending the period of heating, nor was it affected appreciably when different samples of the materials were used. It was, however, raised to 40 per cent. of the salicylic acid used by the addition of a molecular proportion of phenol to the mixture. Thus a mixture of 50 grams of salicylic acid and 50 grams of phenol, when boiled for six hours with 100 grams of acetic anhydride and distilled, yielded 20 grams of xanthone. In all these cases the yield is extremely poor when no acetic anhydride is employed, and acetic acid has no effect at all.

When *o*-acetoxybenzoic acid is similarly boiled either alone or with acetic anhydride, it yields xanthone equivalent to 20 per cent. of its salicylic acid content.

##### *Mononitroxanthones.*

*1-Nitroxanthone.*—*m*-Nitrophenol (1.6 grams) was dissolved in 20 c.c. of methyl alcohol containing 0.4 gram of sodium. *o*-Chlorobenzoic acid (1.5 grams) was then added to the solution, and also a trace of copper powder. The alcohol was evaporated, and the dry, brown substance began to soften at about 100°; the temperature of the bath was raised to 110°, when the contents of the vessel melted to a dark brown liquid which solidified partly at about 140°. When cool, the contents were powdered and heated on a steam-bath for ten minutes with 15 c.c. of concentrated sulphuric acid. The solution was cooled, poured into water, and the precipitate collected. The substance crystallised from alcohol in slender, brown needles melting at 210° (Found: N=5.99.  $C_{10}H_7O_4N$  requires N=5.80 per cent.).

It shows no fluorescence in concentrated sulphuric acid solution, but gives a yellow colour only.

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*1-Nitroxanthone.*—*m*-Nitrophenol (1.6 grams) was dissolved in 20 c.c. of methyl alcohol containing 0.4 gram of sodium. *o*-Chlorobenzoic acid (1.5 grams) was then added to the solution, and also a trace of copper powder. The alcohol was evaporated, and the dry, brown substance began to soften at about 100°; the temperature of the bath was raised to 110°, when the contents of the vessel melted to a dark brown liquid which solidified partly at about 140°. When cool, the contents were powdered and heated on a steam-bath for ten minutes with 15 c.c. of concentrated sulphuric acid. The solution was cooled, poured into water, and the precipitate collected. The substance crystallised from alcohol in slender, brown needles melting at 210° (Found: N=5.99.  $C_{13}H_7O_2N$  requires N=5.80 per cent.).

It shows no fluorescence in concentrated sulphuric acid solution, but gives a yellow colour only.

*2-Nitroxanthone*.—*p*-Nitrophenol (4.2 grams) was dissolved in 20 c.c. of methyl alcohol, and 0.7 gram of metallic sodium was then added to the solution. When it was clear, 4.7 grams of *o*-chlorobenzoic acid were added, and a trace of copper powder was introduced as a catalyst. The alcohol was evaporated off slowly, and then the temperature of the bath was raised very slowly to 140°, when the orange-brown, hard mass melted to a viscous liquid of the same colour. After some twenty minutes, the colour began to change, and the liquid then became converted into a greyish-red, jelly-like substance. The temperature was very cautiously raised to 160°, when the dark-coloured substance solidified. The whole mass, however, bursts into flame at about this temperature if more than one atomic proportion of sodium is taken or if the temperature is raised suddenly. The substance, when cool, was powdered and heated on a steam-bath with 50 c.c. of concentrated sulphuric acid for twenty-five minutes. The solution, when cool, was poured into water, and the precipitate was collected (7 grams). The substance crystallised from alcohol in slender, brown needles melting at 200° and dissolving in sulphuric acid with a greenish-blue fluorescence (Found: N=5.56.  $C_{13}H_7O_4N$  requires N=5.80 per cent.).

*3-Nitroxanthone*.—This was first prepared by Ullmann (*loc. cit.*) by the condensation of 2-chloro-4-nitrobenzoic acid with phenol. It has, however, been possible to obtain this compound directly from xanthone by nitration in the following way. Six grams of xanthone were dissolved in 12 c.c. of concentrated sulphuric acid, and 1.4 c.c. of nitric acid (D 1.500) added with shaking. Much heat was developed. The solution was kept overnight and then poured into water, the precipitate (about 7 grams) being collected and washed with water. About 2 grams of the substance, which did not dissolve in alcohol, consisted of  $\beta$ -dinitroxanthone. From the alcoholic solution, yellowish-white needles were obtained, which were found to contain traces of xanthone. The nitro-compound was purified by further crystallisation from alcohol. Traces of xanthone were found still to be associated with it, and could be removed only with very great difficulty, because of the almost equal solubility of each of these compounds in alcohol.

On reduction, traces of xanthone were removed, as this is insoluble in dilute hydrochloric acid, whereas the amino-compound was obtained as hydrochloride in the solution. The free amino-compound, isolated by precipitation with ammonia, melts at 232° (as given by Ullmann, *loc. cit.*).

When 1 gram of 3-nitroxanthone is dissolved in 10 c.c. of con-

centrated sulphuric acid and 5 c.c. of nitric acid (D 1.42) are added to the solution and the mixture kept overnight, a trinitro-xanthone is obtained. This compound is described subsequently.

3-Nitro-xanthone dissolves in sulphuric acid with a blue fluorescence much stronger than that shown by xanthone itself.

*4-Nitro-xanthone*.—A mixture of 50 grams of salicylic acid and 50 grams of *o*-nitrophenol was boiled with 100 grams of acetic anhydride for ten hours and then distilled. Some tarry matter passed over at a very high temperature. This was boiled with alcohol with the addition of animal charcoal, and from the filtrate about 2.5 grams of yellow needles were obtained melting at 127° (Found: N=5.71.  $C_{13}H_7O_4N$  requires N=5.80 per cent.). The compound dissolves in sulphuric acid with a green colour and without fluorescence. It is remarkable that no xanthone could be traced in the distillate. Attempts were made to condense *o*-nitrophenol with *o*-chlorobenzoic acid by Ullmann's method, but without success.

#### *Dinitroxanthones.*

$\alpha$  and  $\beta$ -Dinitroxanthones are ordinarily obtained by nitrating xanthone with a mixture of nitric and sulphuric acids. They have also been prepared by nitrating xanthone with fuming nitric acid alone.

When 2 grams of xanthone are dissolved in 5 c.c. of nitric acid (D 1.500) and the solution is heated on a water-bath for about ten minutes, fine needles of  $\beta$ (or 2:7)-dinitroxanthone precipitate, and from the solution  $\alpha$ -dinitroxanthone is obtained by precipitation with water and purification with nitric acid. Similar results are obtained with weaker nitric acid (D 1.42), but the quantity of acid should be proportionately greater, namely, 10 c.c. for each gram of xanthone, and the mixture should be heated for about three hours.

$\beta$ (or 2:7)-*Dinitro-xanthone*.—One gram of 2-nitro-xanthone was dissolved in a cold mixture of 25 c.c. of nitric acid (D 1.42) and 25 c.c. of concentrated sulphuric acid. The solution was kept overnight, and then poured into water. The yellow precipitate (1.5 grams) was collected and crystallised from nitric acid, when it was obtained in white needles melting at 254°. When mixed with 2:7-dinitroxanthone (m. p. 262°), it melted at 254—260° (Found: N=9.79. Calc.: N=9.81 per cent.). From the nitric acid filtrate a trinitro-xanthone was obtained (see below).

$2:4$ -*Dinitroxanthone*.—This compound was prepared by Mayer (*loc. cit.*) by the condensation of sodium phenoxide and 2-chloro-3:5-dinitrobenzoic acid. It can also be prepared by condensing 2:4-dinitrophenol with *o*-chlorobenzoic acid in the following way.

2:4-Dinitrophenol (1.25 grains) and sodium (0.17 gram) are dissolved in methyl alcohol (20 c.c.), and to the clear solution *o*-chlorobenzoic acid (1.2 grams) and a trace of copper powder added. After evaporating the alcohol, the yellow residue melts partly at 160° and solidifies in a few minutes. It is cooled, powdered, and heated again to 160°, when it melts and resolidifies as before. This process is repeated about ten times, when the condensation is complete, and the substance does not melt on heating to 160°. If the temperature of the bath is raised with the view of completing the reaction in one operation, the whole mass suddenly inflames at about 200° without melting. After the completion of the condensation, the powdered substance is heated on a steam-bath with 20 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution is poured into water and the precipitate is collected. The substance, when decolorised with animal charcoal in alcoholic solution, crystallises from this solvent in yellow needles melting at 206° (Found: N=9.91. Calc.: N=9.81 per cent.).

*Trinitroanthones.*

*2:3:7-Trinitroanthone*.—When 2-nitroanthone was nitrated (see above), 2:7-dinitroanthone was the first product, and from the nitric acid filtrate a yellowish-white precipitate was obtained by adding water. After being boiled with alcohol to remove impurities, it melted at 203° (Found: N=12.74.  $C_{18}H_5O_3N_3$  requires N=12.63 per cent.). The same trinitroanthone was obtained when 6 grams of 2:7-dinitroanthone were dissolved in 50 c.c. of concentrated sulphuric acid, 1.2 c.c. of nitric acid (D 1.500) added, and the solution was heated on a water-bath for twenty-four hours. The unchanged dinitro-compound was crystallised from nitric acid and collected, and the filtrate on concentration gave yellow needles melting at 205°.

This compound was also obtained by nitrating 3-nitroanthone.

*Dinitromonoaminoanthone*.—The trinitro compound was reduced with alcoholic ammonium sulphide, and the product separated from alcohol as a dark brown powder melting and decomposing at 230° (Found: N=14.55.  $C_{13}H_7O_6N_3$  requires N=14.43 per cent.).

*Dinitroanthoneazo-β-naphthol*.—The dinitroaminoanthone was diazotised in the usual way and coupled with β-naphthol. The azo-compound separates from alcohol as a dark red, amorphous powder melting at 270° (Found: N=12.25.  $C_{23}H_{12}O_7N_4$  requires N=12.28 per cent.).

*Trinitroxanthone*.—Two grams of xanthone were dissolved in 7 c.c. of concentrated sulphuric acid with the aid of heat, and 2 c.c. of nitric acid (D 1.500) added to the cooled solution. The latter was then kept over the steam-bath, when a copious precipitate appeared in a few minutes consisting of yellow, glistening needles, which were filtered through asbestos and washed with dilute nitric acid, and finally with water. The substance dissolves freely in cold nitric acid (D 1.42). It melts at 225°, and is not identical with the trinitro-compound previously mentioned (Found: N=12.72.  $C_{13}H_5O_5N_3$  requires N=12.63 per cent.).

*Dinitromonoaminoxanthone*.—This was obtained by reducing the trinitro-derivative with alcoholic ammonium sulphide in the usual way. It was obtained as a yellow powder melting at 290° (Found: N=14.47.  $C_{13}H_7O_6N_3$  requires N=14.43 per cent.).

#### *Tetranitroxanthones.*

*1-Tetranitroxanthone*.—This compound was obtained by dissolving 0.5 gram of 1-nitroxanthone in 5 c.c. of concentrated sulphuric acid and adding 2.5 c.c. of nitric acid (D 1.42). The solution, on keeping overnight, deposited yellowish-white needles melting at 250°. It is evidently different from  $\alpha_1$ -,  $\alpha_2$ -, or  $\beta$ -tetranitroxanthones, which do not melt at 300° (Found: N=14.64.  $C_{13}H_4O_{10}N_4$  requires N=14.89 per cent.).

*4-Tetranitroxanthone*.—Half a gram of 4-nitroxanthone was dissolved in 5 c.c. of concentrated sulphuric acid, and 2.5 c.c. of nitric acid (D 1.42) were then added gradually with shaking. At the first addition of nitric acid a violent reaction ensued, and the reaction vessel was cooled. After keeping the mixture for a few days, a reddish-yellow precipitate was obtained, which did not melt at 300° (Found: N=15.32.  $C_{13}H_4O_{10}N_4$  requires N=14.89 per cent.).

*4<sub>z</sub>-Tetranitroxanthone*.—When the filtrate from the nitro-compound described above was added to water, there was obtained a brown powder, which could not be crystallised from alcohol, benzene, or nitric acid. It melts and decomposes at 200° (Found: N=14.70.  $C_{13}H_4O_{10}N_4$  requires N=14.89 per cent.).

*$\alpha_1$ -Tetranitroxanthone*.—Thirteen grams of  $\alpha$ -dinitroxanthone were added to a mixture of 150 c.c. of concentrated sulphuric acid and 150 c.c. of nitric acid (D 1.42). The mixture was heated on a steam-bath, when a clear solution was obtained in a few minutes and shining, yellowish white crystals (10.7 grams) separated in about six hours. These did not melt at 300° (Found: N=14.79.  $C_{13}H_4O_{10}N_4$  requires N=14.89 per cent.). This substance when

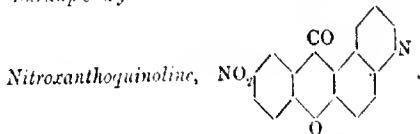
heated with bromine and a trace of iodine in a sealed tube gives dibromodinitroxanthone (m. p. 265°) (see this vol., pp. 998-999).

$\alpha_2$ -Tetranitroxanthone.—From the filtrate from the preceding compound, crystals, in the form of broken plates, were obtained by adding water. They also do not melt at 300° (Found: N=14.69.  $C_{13}H_4O_{10}N_4$  requires N=14.89 per cent.).

This substance, when treated similarly with bromine, gives a tetrabromoxanthone (m. p. 255°).

$\beta_2$ -Tetranitroxanthone.—Ten grams of 2:7-dinitroxanthone were added to a mixture of 150 c.c. of concentrated sulphuric acid and 150 c.c. of nitric acid (D 1.42). The mixture was heated for about six hours, when bright yellowish-white crystals (9 grams) were precipitated. The compound was found to be identical with  $\alpha_1$ -tetranitroxanthone, as both these substances gave the same dibromodinitroxanthone when treated similarly with bromine. From the filtrate, 3.5 grams of shining, white, broken plates were obtained, which did not melt at 300° (Found: N=14.69.  $C_{13}H_4O_{10}N_4$  requires N=14.89 per cent.). When this substance is heated with bromine exactly in the same way as the other tetra-nitro-compounds, a hexabromoxanthone is obtained, which melts at 285°.

*Skraup's Synthesis with Dinitroxanthone.*



Three grams of 2:7-dinitroxanthone were dissolved in 5 c.c. of concentrated sulphuric acid, and 12 c.c. of glycerol added. The addition of the latter precipitated the nitro-compound. The mixture was heated in a paraffin-bath, and at about 140° it began to froth, when the flask was shaken and the temperature lowered to 110°. Heating was continued for four hours at about 120°, and then for a further two hours at about 140°, when a semi-solid mass resulted. This was then heated for a further three hours until the black mixture became solid. The mass was powdered, and the crude product boiled with water and filtered. The filtrate, on being rendered alkaline, gave an orange-red, colloidal precipitate, which settled on keeping overnight and was collected. The substance separates from alcohol as an orange-red powder, which sinters at 200° and melts at 205-210° (Found: N=9.75.  $C_{16}H_8O_4N_2$  requires N=9.59 per cent.). The substance dissolves readily in alcohol, acids, or excess of alkali hydroxide.

*Xanthhydrols.*

*α-Dinitroxanthhydrol.*—*α*-Dinitroxanthone (2·5 grams) was suspended in 100 c.c. of methyl alcohol, and 1 gram of sodium added in small pieces with shaking. The colour of the mixture became first orange, and finally deep red. It was boiled under reflux for half an hour, when a clear, dark red solution was obtained; the boiling was continued for a further period of one and a-half hours, and the solution filtered hot. A yellowish-brown precipitate was obtained on acidifying the solution with hydrochloric acid, and this crystallised from acetic acid in brown needles melting at 185° (Found: N=10·11.  $C_{13}H_8O_6N_2$  requires N=9·72 per cent.). The substance dissolves in alcohol and in cold dilute alkali hydroxide, in the latter solvent with a yellow colour. Its solution in concentrated sulphuric or hydrochloric acid is pale yellow, and in nitric acid it dissolves with a pink coloration. When heated with glacial acetic acid, it dissolves to an orange-red solution.

*β*(or 2:7)-*Dinitroxanthhydrol.*—This substance was obtained by treating 2·5 grams of 2:7-dinitroxanthone with sodium and methyl alcohol, as in the case of the *α*-dinitro-compound. It crystallised from alcohol in slender, yellowish-white needles melting and decomposing at 196° (Found: N=9·65.  $C_{13}H_8O_6N_2$  requires N=9·72 per cent.). The substance dissolves in cold aqueous alkali hydroxide as well as in concentrated sulphuric acid with a yellow coloration, and in concentrated hydrochloric acid to a pale yellow solution.

Each of these dinitroxanthhydrols, when boiled with a mild oxidising agent, such as a dilute solution of hydrogen peroxide or potassium permanganate, is converted into the corresponding dinitroxanthone.

*Chlorosanthones.*

*1-Chloroxanthone.*—*o*-Chlorobenzoic acid (1·6 grams), *m*-chlorophenol (1·4 grams), and sodium (0·4 gram) were dissolved in methyl alcohol (10 c.c.), a trace of copper powder being added as a catalyst. The solution was heated on an oil-bath, and the alcohol evaporated, when the substance melted at about 200° and solidified, at about 215°. It was cooled, powdered, and heated on a steam-bath with 15 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution was poured into water, and the precipitate collected. The substance crystallised from aqueous alcohol in white needles melting at 100°. It dissolves in sulphuric acid with a green fluorescence. In this synthesis, either 1 chloro-

xanthone or 3-chloroxanthone or both may possibly be formed, but only one product was obtained. As it differed from 3-chloroxanthone, which melts at 130°, it must be 1-chloroxanthone (Found: Cl=15.46.  $C_{13}H_7O_2Cl$  requires Cl=15.40 per cent.).

*1-Anilinoxanthone*.—One gram of the substance described above was boiled with 3 c.c. of aniline and a trace of copper powder for six hours. A blue precipitate was obtained by pouring the solution into water acidified with hydrochloric acid. After being purified by extraction with alcohol, it melted at 120—125° (Found: N=4.86.  $C_{19}H_{12}O_2N$  requires N=4.87 per cent.).

*1-Chlorotetranitroxanthone*.—Half a gram of 1-chloroxanthone was dissolved in 7 c.c. of concentrated sulphuric acid, and 5 c.c. of nitric acid (D 1.42) were added to the solution with shaking. The solution was kept overnight, when white needles were obtained, which melted at 195° (Found: N=13.70.  $C_{13}H_2O_10N_4Cl$  requires N=13.69 per cent.). From the filtrate, a white precipitate was obtained, which was too small in amount for any detailed examination.

*2-Chloroxanthone*.—*p*-Chlorophenol (1.4 grams) was dissolved in methyl alcohol (10 c.c.), and sodium (0.4 gram) and *o*-chlorobenzoic acid (1.6 grams) and a trace of copper powder were added to the solution. The alcohol was evaporated, and the viscous, semi-solid mass was heated to 140°, and kept at that temperature for half an hour, when it darkened. It dried to a black solid mass at 150°. The temperature was further raised to 200°, and then the substance was cooled, powdered, and heated on a water-bath with 15 c.c. of concentrated sulphuric acid for fifteen minutes. When cool, the solution was poured into water; the precipitate was collected, crystallised from alcohol, and obtained in white needles melting at 165° (Ullmann, *loc. cit.*, gives 171°). It dissolves in sulphuric acid with a blue fluorescence (Found: Cl=15.72. Calc.: Cl=15.40 per cent.).

*2-Chlorotetranitroxanthone*.—This compound was obtained by nitrating 2-chloroxanthone with concentrated sulphuric and nitric acids. For each gram of substance, 10 c.c. of sulphuric acid and 7 c.c. of nitric acid were used. The substance was obtained in slender, yellowish-white needles melting at 205° (Found: N=13.73.  $C_{13}H_2O_10N_4Cl$  requires N=13.69 per cent.).

*4-Chloroxanthone*.—This substance was obtained by the condensation of *o*-chlorobenzoic acid with *o*-chlorophenol in the manner described in the syntheses of 1-chloroxanthone. It crystallised from alcohol in slender, white needles melting at 130°. It dissolves in concentrated sulphuric acid with a green fluorescence (Found: Cl=15.36.  $C_{13}H_7O_2Cl$  requires Cl=15.40 per cent.).

*4-Chlorotrinitroxanthone*.—This compound was obtained by

nitrating 4-chloroxanthone with concentrated sulphuric and nitric acids. For each gram of the substance, 5 c.c. of sulphuric acid and 4 c.c. of nitric acid were used. Brownish-yellow needles were obtained on keeping the reaction mixture overnight. The substance melts at 235° (Found: N=11.14.  $C_{13}H_4O_6N_3Cl$  requires N=11.49 per cent.).

*4-Chlorodinitroxanthone*.—This substance was obtained from the filtrate of the trinitro-compound as a pale yellow powder melting and decomposing at 195—200° (Found: N=8.81.  $C_{13}H_4O_6N_2Cl$  requires N=8.73 per cent.).

*Dichloroxanthone*.—Xanthone (7.5 grams) was dissolved in acetic acid (50 c.c.) with the aid of heat. A current of dry chlorine was passed into the solution, which was kept warm by heating the reaction vessel over a steam-bath until approximately one molecular proportion of chlorine was absorbed. A trace of iodine was used as a catalyst. The product (10 grams) crystallised from alcohol in slender, white needles melting at 225° (Found: Cl=26.86.  $C_{13}H_4O_6Cl_2$  requires Cl=26.80 per cent.). The substance dissolves in concentrated sulphuric acid with a strong green fluorescence. From the alcoholic filtrate from the dichloroxanthone another product mixed with it was obtained, which appeared to be 3-chloroxanthone from its melting point and chlorine content, but it has not yet been possible to purify it completely.

*Dichlorodinitroxanthone*.—The dichloro-compound was nitrated in the cold with a mixture of equal volumes of nitric (D 1.42) and concentrated sulphuric acids (100 c.c. for each gram of the substance). On keeping the solution overnight, yellow needles were obtained, which melted at 210° (Found: N=8.10.  $C_{13}H_4O_6N_2Cl_2$  requires N=7.88 per cent.).

#### *Bromo-xanthones.*

*2-Bromoxanthone*.—*p*-Bromophenol (2.5 grams) and sodium (0.6 gram) were dissolved in methyl alcohol (15 c.c.) and *o*-chlorobenzoic acid (2.3 grams) and a trace of copper powder were added to the solution. It was heated to 160°, when a hard, black mass was obtained. The temperature was raised to 220°, but the substance did not fuse. It was cooled, powdered, and heated over a steam-bath with 25 c.c. of concentrated sulphuric acid for twenty-five minutes. When cool, the solution was poured into water and the precipitate collected. It crystallised from aqueous alcohol in brown needles melting at 150°, and dissolved in sulphuric acid with a yellow colour, but no fluorescence (Found: Br=29.00.  $C_{13}H_4O_6Br$  requires Br=29.16 per cent.). 2-Bromoxanthone is also obtained when xanthone is brominated in concentrated

sulphuric acid solution with bromine and a trace of iodine. It is very difficult, however, to isolate the substance in a pure condition, because the last traces of either xanthone or dibromoxanthone, which are always associated with this compound, cannot easily be removed.

*2-Bromo- $\alpha$ -tetranitroxanthone.*—2-Bromoxanthone (0.7 gram) was dissolved in concentrated sulphuric acid (10 c.c.), and nitric acid (5 c.c. of D 1.42) then added gradually to the solution with shaking. No precipitate was formed after keeping it for a few days. The solution was poured into water, and the precipitate was boiled with alcohol, in which it partly dissolved. From the alcoholic solution, the substance was obtained in slender, brown needles melting at 210° (Found: N=12.02.  $C_{13}H_8O_4N_4Br$  requires N=12.31 per cent.).

*2-Bromo- $\beta$ -tetranitroxanthone.*—The residue of the nitro-compound described above was dissolved in benzene, and crystallised from this solution in brown needles melting at 270° (Found: N=12.21.  $C_{13}H_8O_4N_4Br$  requires N=12.31 per cent.). When 2-bromoxanthone was heated with bromine (1 or 2 mols.) in acetic acid solution and a trace of iodine, over a sand-bath, a dibromo-compound was obtained which melted at 212°. This compound was identified as 2:7-dibromoxanthone by the method of mixed melting points. It is also obtained by brominating xanthone with bromine, using iron filings as a catalyst.

*4-Bromoxanthone.*—This compound was obtained by condensing *o*-bromophenol with *o*-chlorobenzoic acid in the usual way. It crystallised from alcohol in greyish-white needles melting at 140°. It shows no fluorescence in sulphuric acid solution (Found: Br=29.28.  $C_{13}H_7O_2Br$  requires Br=29.16 per cent.).

*4-Bromodinitroxanthone.*—4-Bromoxanthone was dissolved in the requisite amount of concentrated sulphuric acid in the cold, and nitric acid (D 1.42) was added to the solution (20 c.c. for each gram of the substance). On keeping the solution overnight, yellowish-white needles were obtained, which melted at 295° (Found: N=8.09.  $C_{13}H_8O_4N_2Br$  requires N=7.67 per cent.).

The author takes this opportunity of expressing his thanks to Professor J. F. Thorpe and Dr. M. A. Whiteley for their kind encouragement, and to the Van't Hoff Memorial Fund Committee and to the Chemical Society for Research Grants which met part of the expenses.

CXIX.—*Complex Metallic Ammines. Part IV. cis-Sulphoacetato-, cis-Methionato- and cis-Dimethylmalonato-diethylenediaminecobaltic Salts.*

By THOMAS SLATER PRICE and JAMES COOPER DUFF.

WERNER (*Annalen*, 1911, **386**, 79) has shown that complex cobalt-ammines containing the malonato radicle are easily prepared, but he was of the opinion (*ibid.*, pp. 26, 81) that complexes containing a higher number of atoms to the ring than six could not be obtained. Price and Brazier (T., 1915, **107**, 1367) showed, however, that when a sulphur atom forms one of the components of the ring, an eight-ring can be obtained, and were successful in preparing *cis*-sulphonyldiacetato-diethylenediaminecobaltic salts. The part played by the sulphur in enabling such compounds to be isolated is not clear. It may be that the presence of sulphur in the acid radicle enabled ring-formation to take place readily, or it may be that the compounds could be isolated, because they were readily obtained in the crystalline form, whereas the attempts by Werner to obtain products containing the succinato- and other radicles only gave rise to uncyclisable syrups or glasses. It was therefore of interest to investigate the behaviour of other dibasic acids containing sulphur, and the present communication details the results obtained with sulphoacetic acid,



and with methionic acid,  $\text{CH}_2(\text{SO}_3\text{H})_2$ , both of which give rise to crystalline compounds.

In a previous paper (Price and Brazier, T., 1915, **107**, 1713) it has been shown that malonic acid forms an additive compound with dichlorodiethylenediaminecobaltic hydrogen malonate, namely,  $\text{Cl}_2\text{Co}(\text{en})_3\text{H}_2\text{A}, \text{H}_2\text{A}=\text{CH}_2(\text{CO}_2\text{H})_2$ , but that the substituted malonic acids do not give rise to such additive compounds, and a tentative explanation of the results obtained was advanced. It was therefore of interest to ascertain whether the substituted malonic acid residue could be introduced into the cobalt complex, giving compounds similar to the malonato-compounds, or whether some such steric hindrance as is postulated in the aforementioned paper prevented their formation. The first experiments were made with dimethylmalonic acid, and we have been successful in preparing dimethylmalonato-diethylenediaminecobaltic salts. The other substituted malonic acids have not yet been investigated, but owing to the fact that one of us (T.S.P.) is taking up other duties, it is considered advisable to publish the results hitherto obtained.\*

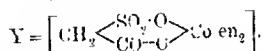
\* These researches are being continued by Mr. Duff (T.S.P.).

The fact that the dimethylmalonic acid residue can be introduced into the nucleus does not necessarily invalidate the explanation given previously of the formation of additive compounds, since, as will be seen in the experimental part, a higher temperature than the ordinary was used, whereby the formation of a ring complex may be greatly facilitated.

As will be seen later, sulphoacetic and methionic acids do not form additive compounds with their dichlorodiethylenediamine-cobaltic acid salts, thus differing markedly from their analogue, malonic acid. No explanation of this is offered at present, since further work is necessary.

#### EXPERIMENTAL.

*cis-Sulphoacetato:diethylenediaminecobaltic Salts*, YX, where



To obtain the *bromide*, YBr. 5 grams of carbonatodiethylenediaminecobaltic bromide were dissolved in 80 c.c. of warm water, and a solution of 2.19 grams of sulphoacetic acid in 20 c.c. of water was added. Evaporation of the mixed solution on the water-bath to a small bulk only resulted in a very poor yield of crystals. It was found best to heat the solution, after the evolution of carbon dioxide had slackened, in a closed bottle at 105° for four hours, and then evaporate to small bulk on the water-bath. After remaining in the ice-chest overnight, the anhydrous bromide separated in small, carmine-red plates, which were collected and washed with water and alcohol. The yield was 2.4 grams, but a further small quantity was obtained by evaporation of the filtrate (Found: Co = 14.87; Br = 20.08.  $\text{C}_6\text{H}_{18}\text{O}_3\text{N}_4\text{BrSCo}$  requires Co = 14.85; Br = 20.15 per cent.).

The *nitrate*, YNO<sub>3</sub>, was obtained in brick-red, elongated plates by precipitating a solution of 2 grams of the bromide in 50 c.c. of water with the equivalent quantity (0.86 gram) of silver nitrate. After shaking for one hour, the silver bromide was collected and the filtrate evaporated to low bulk on the water-bath. The crystals of the nitrate separated slowly on keeping in the ice-chest. Yield, 0.8 gram (Found: Co = 15.39; N = 18.24.  $\text{C}_6\text{H}_{18}\text{O}_3\text{N}_3\text{SCo}$  requires Co = 15.56; N = 18.47 per cent.).

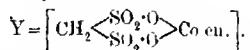
The *thiocyanate*, YSCN, was obtained by adding 1.5 grams of solid potassium thiocyanate to a saturated solution containing 3 grams of the bromide. The potassium thiocyanate dissolved, and, after leaving overnight in the ice-chest, microscopic, brick-red crystals of the complex thiocyanate separated (Found: Co = 15.62;

$N = 18.91$ .  $C_7H_{18}O_5N_5S_2Co$  requires  $Co = 15.73$ ;  $N = 18.67$  per cent.).

The *platinichloride*,  $Y_2PtCl_6$ , was prepared by filtering a saturated solution containing 2 grams of the bromide into a 5 per cent. solution of chloroplatinic acid. Microscopic, pale brown crystals slowly separated; these were collected after two hours and washed with alcohol and ether, and dried in a vacuum desiccator [Found:  $Co = 11.11$ ;  $Pt = 18.95$ .  $(C_6H_{18}O_5N_4SCo)_2PtCl_6$  requires  $Co = 11.32$ ;  $Pt = 18.72$  per cent.].

The *hydrogen sulphoacetate*,  $YSO_3CH_2CO_2H$ , was obtained by dissolving 6 grams of the carbonato-bromide in 120 c.c. of water and shaking the cooled solution with 4 grams of freshly prepared moist silver oxide for half an hour. The product was then filtered into an aqueous solution of 5.25 grams of sulphoacetic acid, the proportions being two molecules of the acid to one of the carbonato-bromide. The resulting solution was evaporated to low bulk on the water-bath, and, after keeping overnight in the ice-chest, deposited microscopic, pink crystals, which dissolve readily in cold water. Yield, 2.8 grams (Found:  $Co = 12.79$ ;  $N = 12.23$ .  $C_5H_{21}O_{10}N_4S_2Co$  requires  $Co = 12.93$ ;  $N = 12.28$  per cent.).

*cis-Methionatoethylenediaminecobaltic Salts*,  $YX$ , where



The *bromide*,  $YBr_2H_2O$ , was only obtained after several attempts had been made to prepare it from the carbonato-bromide according to the method used by Price and Brazier in making sulphonyldiacetatoethylenediaminecobaltic bromide (*loc. cit.*). It was found that on mixing solutions of the carbonato-bromide and methionic acid in equivalent quantities and evaporating on the water-bath, pink, microscopic crystals separated in increasing quantity as evaporation proceeded. These crystals, however, contained no bromine, and were later identified as the methionato-methionate (Found:  $Co = 13.20$ ). On further evaporation, the mother liquor gave no crystals of the bromide, a syrupy liquid resulting which contained some unused carbonato-bromide. To avoid this formation of the methionate, it was found best to dissolve 5 grams of the carbonato-bromide in 120 c.c. of water and add a solution of 2.73 grams of methionic acid in 40 c.c. of water. The whole solution was then well boiled for twenty minutes, keeping the volume at about 150 c.c. by the addition of boiling water.\* After evaporating the resulting solution on the water-bath to low

\* This method of treatment has already given successful results in the case of succinato-compounds, which will be dealt with in a later paper by one of us.

bulk and keeping for two days in the ice-chest, the pure methionato-bromide separated in purplish-red plates, which were collected and washed with water and alcohol. Yield, 1·4 grams [Found: Co=12·50; Br=17·02; S=13·28; H<sub>2</sub>O (at 100°)=7·74. C<sub>5</sub>H<sub>15</sub>O<sub>6</sub>N<sub>4</sub>BrS<sub>2</sub>Co,2H<sub>2</sub>O requires Co=12·57; Br=17·04; S=13·64; H<sub>2</sub>O=7·68 per cent.].

The *nitrate*, YNO<sub>3</sub>.2H<sub>2</sub>O, was obtained by shaking for one hour a solution of 3 grams of the hydrated bromide in 60 c.c. of water with the equivalent quantity (1·08 grams) of silver nitrate. The silver bromide was then collected and the filtrate evaporated to low bulk on the water-bath. After keeping for several days in the ice-chest, the nitrate separated in carmine-red, elongated plates. Yield, 0·5 gram [Found]: Co=13·42; N=15·76; H<sub>2</sub>O (at 110°)=7·94. C<sub>5</sub>H<sub>15</sub>O<sub>6</sub>N<sub>3</sub>S<sub>2</sub>Co,2H<sub>2</sub>O requires Co=13·08; N=15·52; H<sub>2</sub>O=7·98 per cent.].

The *thiocyanate*, YSCN, was prepared by adding 1·5 grams of solid potassium thiocyanate to a saturated solution of 3 grams of the methionato-bromide. After keeping overnight, the complex thiocyanate separated in microscopic, dark red crystals (Found: Co=14·68; N=17·40. C<sub>5</sub>H<sub>15</sub>O<sub>6</sub>N<sub>3</sub>S<sub>3</sub>Co requires Co=14·33; N=17·03 per cent.).

The *platinichloride*, Y<sub>2</sub>PtCl<sub>6</sub>, was obtained by filtering a saturated solution of the methionato-bromide into a 5 per cent. solution of chloroplatinic acid. Microscopic, light brown crystals readily separated, which were washed with alcohol and ether and dried in a vacuum desiccator [Found: Co=10·34; Pt=17·83. (C<sub>5</sub>H<sub>15</sub>O<sub>6</sub>N<sub>4</sub>S<sub>2</sub>Co)<sub>2</sub>PtCl<sub>6</sub> requires Co=10·58; Pt=17·52 per cent.].

The hydrogen methionate could not be obtained, although the same method was used that has always been successful in similar cases. When two molecular proportions of methionic acid in solution were mixed with one of the carbonato-base, the crystals which separated on evaporation always proved to be the normal methionate. When this was dissolved in a boiling solution of methionic acid, only the unchanged salt separated on evaporation. The *normal methionate*, CH<sub>3</sub>(SO<sub>3</sub>Y)<sub>2</sub>, was prepared by dissolving 7 grams (2 mols.) of the carbonato-bromide in 120 c.c. of warm water, shaking for half an hour with 3·8 grams of freshly prepared silver oxide, and filtering from the silver bromide into a solution containing 5·78 grams (3 mols.) of methionic acid. The mixed solution was then evaporated to low bulk on the water-bath. Complete separation of the normal methionate in pink, microscopic crystals only occurred when a little water was added to the resulting syrup and the whole well stirred. The yield was 7·3 grams. The salt is almost insoluble in cold water, but dis-

solves readily in hot water (Found: Co=13.56; N=12.64; S=21.37.  $C_{11}H_{38}O_{18}N_8S_6Co_3$  requires Co=13.41; N=12.72; S=21.82 per cent.).

The normal methionate dissolves readily in cold dilute ammonia or sodium carbonate solution, but is not reprecipitated on acidifying. Barium hydroxide solution also dissolves it, giving a blood-red solution, from which barium methionate separates on keeping. Excess of barium hydroxide is required for solution, so that the reaction cannot be used as a method for obtaining the methionato-hydroxide, and hence the chloride. When the normal methionate is heated with a solution of barium chloride, a blood-red solution results, from which barium methionate separates on cooling. The filtrate from these crystals changes to a purple colour on evaporation, and small, purple crystals of *cis*-dichlorodiethylenediaminecobaltic chloride separate after a time (Found: Co=20.86. Calc.: Co=20.67 per cent.).

Concentrated solutions of the methionato bromide do not give any precipitate when mixed with a solution of mercuric bromide in potassium bromide solution. On boiling the resulting solution, however, there is at once formed the green double salt of mercuric bromide and the *trans*-dibromo-bromide,  $[Br_2Coen_2]Br_2HgBr_2$  which separates from the hot solution in small, flattened needles (Found: Co=7.47; Br=49.83. Calc.: Co=7.56; Br=51.28 per cent.).

#### *trans*-Dichlorodiethylenediaminecobaltic Salts.

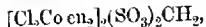
Since both sulphoacetic acid and methionic acid may be considered to be analogues of malonic acid, it was expected that they would give additive compounds with their acid salts of dichlorodiethylenediaminecobalt. This was found not to be the case, however, the substitution of  $\text{CO}_2\text{H}$  by  $\text{SO}_3\text{H}$  thus playing a part which requires further investigation. Price and Brazier (*loc. cit.*, 1737) found that sulphonyldiacetic acid, which contains an  $\text{O}_2\text{C}$  group in place of one of the  $\text{CH}_2$ -groups of glutaric acid, did give rise to such additive compounds.

*trans*-Dichlorodiethylenediaminecobaltic hydrogen sulphoacetate,  $Cl_2Coen_2[SO_3CH_2CO_2H]$ , separates immediately as emerald-green, triated, and elongated plates when 3 grams of the *trans*-dichloro-chloride are stirred into a cold solution of 4.3 grams of sulphoacetic acid in 15 c.c. of water. Yield, 3.1 grams (Found: Co=15.24; Cl=18.37.  $C_6H_{10}O_4N_2Cl_2SCo$  requires Co=15.16; Cl=18.23 per cent.).

*cis*-Sulphoacetatoethylenediaminecobaltic chloride could not be obtained from the above hydrogen sulphoacetate in the same way as oxalatoethylenediaminecobaltic chloride was obtained from the

dichloro-hydrogen oxalate (Price and Brazier, *loc. cit.*, p. 1726). When a solution of the hydrogen sulphoacetate was boiled, the colour changed to the blood-red colour of a *cis*-salt, but on evaporation to small bulk, only green crystals could be separated. Repeated boiling of the solution and evaporation only resulted in the recovery of the green crystals of the unchanged hydrogen sulphoacetate.

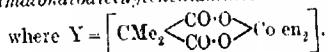
*trans-Dichlorodiethylenediaminecobaltic methionate,*



separated in green, elongated plates when 3 grams of the *trans*-dichloro-chloride were stirred into a cold solution of 4.5 grams of methionic acid in 15 c.c. of water. The separation of crystals was complete after two hours in the ice-chest. Yield, 2.4 grams (Found: Co=17.29; Cl=20.81; S=9.07.  $\text{C}_9\text{H}_{34}\text{O}_6\text{N}_8\text{Cl}_4\text{S}_2\text{Co}_2$  requires Co=17.50; Cl=21.04; S=9.49 per cent.).

When this salt was dissolved in water, together with a molecular proportion of methionic acid, and the solution boiled for fifteen minutes, the colour became deep red, but, on evaporating almost to dryness, only green crystals of the original substance separated. The acid salt could not be obtained.

*cis-Dimethylmalonatodiethylenediaminecobaltic Salts, YX,*



Before commencing the preparation of these salts, the method described by Price and Brazier (*loc. cit.*, p. 1373) for the preparation of *cis*-sulphonyldiacetatodiethylenediaminecobaltic bromide was tested in the case of the malonato-bromide. This consisted in the preparation of the bromide directly by the interaction of one molecular proportion of the carbouato-bromide and one molecular proportion of malonic acid, whereas Werner's method of preparation of such compounds is first to prepare the carbouato-hydroxide and then add two molecular proportions of malonic acid. The method was found to be satisfactory, *cis*-malonatodiethylenediaminecobaltic bromide,  $[\text{CH}_2(\text{CO}_2)_2\text{Co en}_2]\text{Br}, \text{H}_2\text{O}$ , being obtained in large, rhombic, dark red plates, which very readily effloresced on exposure to the air. A freshly prepared specimen, which had slightly effloresced, gave Co=14.18, whereas  $\text{C}_7\text{H}_{18}\text{O}_4\text{N}_4\text{BrCo}, 3\text{H}_2\text{O}$  requires Co=14.21 for  $3\text{H}_2\text{O}$  and Co=14.86 for  $2\text{H}_2\text{O}$ . The anhydrous substance gave Co=16.25, theory requiring Co=16.34 per cent. The corresponding thiocyanate,  $\text{C}_8\text{H}_{18}\text{O}_4\text{N}_5\text{SCo}$ , was readily obtained, and possessed the properties described by Werner (*Annalen*, 1911, 386, 81) (Found: Co=17.19. Calc.: Co=17.39 per cent.).

To obtain *cis-dimethylmalonatoethylenediaminecobaltic bromide*,  $\text{YBr}_2\text{H}_2\text{O}$ , 5 grams of the carbonato-bromide were dissolved in 80 c.c. of warm water and 2.07 grams (1 mol. equiv.) of dimethylmalonic acid added. The resulting solution was evaporated to low bulk on the water-bath, and, after keeping in the ice-chest overnight, crimson-red, microcrystalline plates of the desired salt separated in small quantity. Crystallisation, or, it may be, the introduction of the dimethylmalonato-residue into the complex, takes place very slowly, and it was necessary repeatedly to collect the crystals, wash with alcohol, and evaporate the filtrate and washings in order to obtain any quantity of the salt. The solution cannot be boiled, as was found to be effective in the case of the methionato-compound, owing to decomposition of the dimethylmalonic acid [Found:  $\text{Co}=13.82$ ;  $\text{H}_2\text{O}$  (at  $130^\circ$ ) = 8.44.  $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_2\text{BrCo}_2\text{H}_2\text{O}$  requires  $\text{Co}=13.87$ ;  $\text{H}_2\text{O}=8.47$  per cent. Found:  $\text{Br}=18.54$ .  $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_2\text{BrCo}$  requires  $\text{Br}=18.80$  per cent.].

The *nitrate*,  $\text{YNO}_3\text{.2H}_2\text{O}$ , was prepared by the interaction in solution of equivalent quantities of the bromide (1.134 grams) and silver nitrate (0.4532 gram). After shaking for one hour, the silver bromide was collected and the filtrate evaporated to low bulk on the water-bath. The salt crystallised out very slowly as a crimson, microcrystalline powder or in dark red crusts of indefinite shape \* [Found:  $\text{H}_2\text{O}$  (at  $130^\circ$ ) = 8.85.



requires  $\text{H}_2\text{O}=8.85$  per cent. Found:  $\text{Co}=15.58$ ;  $\text{N}=19.19$ .  $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_2\text{Co}$  requires  $\text{Co}=15.89$ ;  $\text{N}=18.87$  per cent.].

The *chloride*,  $\text{YCl}_3\text{.2H}_2\text{O}$ , was obtained by shaking a solution of the bromide with an excess of freshly precipitated silver chloride, collecting the precipitate, and evaporating the filtrate to low bulk. It separated in microcrystalline prisms, which are very soluble in water [Found:  $\text{H}_2\text{O}$  (at  $130^\circ$ ) = 9.95.†  $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_2\text{ClCo}_2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=9.47$  per cent. Found:  $\text{Co}=16.86$ .  $\text{C}_9\text{H}_{22}\text{O}_4\text{N}_2\text{ClCo}$  requires  $\text{Co}=17.11$  per cent.].

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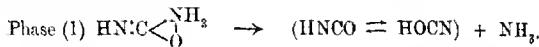
\* Both in the case of the nitrate and the chloride, which are very readily soluble in water, it was difficult to obtain a solution which was just of the right concentration for crystallisation; if too concentrated it formed a viscous mass.

† Only 0.2 gram of the salt was obtained, so that the estimation of the rate of crystallisation could not be repeated. The high value found was probably due to the salt not being quite air-dry, owing to the abnormally damp weather which prevailed at the time:  $3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=13.56$  per cent.

CXX.—*The Constitution of Carbamides. Part XII.*  
*The Decomposition of Urea when Heated in Solution in the Presence of Acids.*

By EMIL ALPHONSE WERNER.

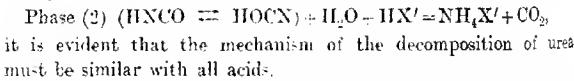
It was shown in Part V of the present series (T., 1918, 113, 84) that the decomposition of urea, when heated in solution with hydrochloric acid, is primarily dependent on the dissociation of "free" urea present, thus:



The hydrolysis of cyanic acid, which follows immediately, proceeds at such a high velocity that both products of dissociation are removed practically as fast as they are generated. Urea fixed as a salt at the outset is thus rapidly "freed" to continue the first phase of the reaction.

Price (T., 1919, 115, 1354) studied the decomposition of urea in the presence of nitric acid, and found that the reaction velocity at 100° was greater than with hydrochloric acid, as compared with the results obtained by Fawsitt (*Zeitsch. physikal. Chem.*, 1902, **41**, 601) with the latter acid. Because the addition of ammonium salts, and of certain salts containing an ion common with the ammonium salt, had a distinct accelerating effect on the decomposition of urea, Price inferred that the author's dissociation theory was apparently not applicable to the change in the presence of nitric acid.

Now, considering the straightforward character of the complete change, the second phase of which is as follows:



The inference drawn by Price is the result of a misunderstanding, since striking proof in support of the dissociation theory has been supplied by his experiments, showing the effect of temperature on the velocity of the decomposition with nitric acid. Thus the values at 100°, 80°, and at 70° were represented by the respective ratios 102, 9:3, and 2:4. Such a great fall in velocity compared with a relatively small fall in temperature is explained by the fact that the dissociation of urea only starts at a fairly rapid rate at about 30°. At 60° it is almost nil (see remarks, Part V, *loc. cit.*, p. 91).

Again, as nitric acid is rather weaker than hydrochloric acid, the theory predicts that the velocity of the reaction should be greater in the presence of the former acid, since the concentration of "free" urea will be greater under similar conditions.

Proof that the amount of urea decomposed is greater\* the weaker the acid is shown by a comparison of the following results obtained in the presence of acetic, nitric, and hydrochloric acids respectively.

The ratio of urea to acid was 1:2 molecular proportions.

The concentration at the outset was urea =  $N/2$ , acid =  $N$ .

The experiments were performed at 100° and under reflux for reasons which have been clearly pointed out before (Part V).

TABLE I.

Time.	Acetic acid. Per cent.	Nitric acid. Per cent.	Hydrochloric acid. Per cent.
1 hour .....	19.5	15.7	13.3
2 hours .....	31.8	25.8	23.2
3 " .....	(a) 41.0	35.0	32.2
4 " .....	(b) 53.4	46.4	40.8
5 " .....	(c) 64.2	57.0	48.4
	(Urea decomposed.)	(Urea decomposed.)	(Urea decomposed.)

The above results were calculated from titrations of the residual acidity at the end of each experiment, with the exception of the values (b) and (c) for acetic acid, which were obtained from determinations of the residual urea, the only trustworthy method in these two cases. As the concentration of ammonium acetate produced during the reaction increased, there was loss of ammonia by its hydrolytic dissociation, whereby residual acidity gave too low a result. Whilst by the titration method (b) was approximately 47, and (c) 51, there was but little difference in the case of (a) when checked by the estimation of residual urea.

Whilst the velocity of phase (1) is directly proportional to the concentration of "free" urea, the amount of the latter in solution at any time is inversely proportional to the strength of the acid present, all other conditions being equal. Hence, after a certain time, a similar condition is attained, no matter what acid may be

\* This is only demonstrable up to a certain point, for an interesting reason. When the concentration of a very weak acid, such as acetic, falls considerably as the reaction proceeds, it is unable to fix ammonia to complete the change of phase (2), with the result that more or less urea is regenerated, thus:  $2\text{HNCO} + \text{H}_2\text{O} \rightleftharpoons \text{CON}_2\text{H}_4 + \text{CO}_2$ . After potassium cyanate was added to an excess of a 2 per cent. solution of acetic acid, urea was detected in the solution.

present, since practically all the residual urea will be "free" when the concentration of acid has fallen very low as a result of its progressive neutralisation. For this reason, the decomposition of all the urea is a very tedious process (compare Fawsitt, *loc. cit.*)

Now, the decomposition of urea in the presence of acids is not an ionic change. "Free" urea is not ionised, and hence the contention that the addition of an ammonium salt, or of any salt, containing an ion common with the acid used should retard the velocity of decomposition does not hold.

The following results were obtained when ammonium nitrate ( $N/4$  at outset) was added in the presence of acetic acid and of nitric acid respectively, and when ammonium chloride ( $N/4$ ) was added in the presence of hydrochloric acid. The concentrations of urea and of acid were as before.

TABLE II.

Time.	Acetic acid + $\text{NH}_4\text{NO}_3$ Per cent.	Nitric acid + $\text{NH}_4\text{NO}_3$ Per cent.	Hydrochloric acid + $\text{NH}_4\text{Cl}$ Per cent.
1 hour .....	22.0	19.9	14.0
2 hours .....	35.1	31.73	29.1
3   , .....	45.4 (Urea decomposed.)	37.40 (Urea decomposed.)	41.2 (Urea decomposed.)

As the reaction progressed, the concentration of ammonium salts increased, and in the case of the nitrate there was appreciable loss of ammonia during three hours' heating, and since the results show sufficiently the general acceleration when compared with the value in table I, experiments were not carried out beyond this period.

The acceleration of the decomposition of urea is here due to the hydrolytic dissociation of the ammonium salts, whereby the velocity of phase (1) is promoted. Whilst the constitution of the simple salts of ammonia is still unsolved, their dissociation\* into acid and ammonia is a well-known fact, their ionisation is a phenomenon which has been assumed but never proved, and, in the author's opinion, it plays no part in the reactions under discussion.

The dissociation of "free" urea is much more sensitive to external conditions than might be supposed; thus, variations in the length and diameter of the reflux tube and in the shape and volume of the flask were sufficient to introduce distinct disturbing effects. Hence two flasks of similar form and volume, and the same reflux tube, were used in the experiments.

\* The presence of moisture being necessary is evidence of its hydrolytic character.

The mode of decomposition of urea in the presence of acids (and of alkalis) is in itself sufficient to throw discredit on the "carbamide" formula.

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CXXI.—*Synthesis of Boranilides. Part I. Boranilide and its Derivatives.*

BY TARINI CHARAN CHAUDHURI.

THE chemical constitution and physiological action of anilides of organic acids have been studied in detail by Gibbs and Hare (*Amer. Chem. J.*, 1890, **11**, 435) and by Gibbs and Reichert (*ibid.*, 1891, **13**, 289).

It was hoped that, if boric acid could be combined with aniline to form boranilide, the latter would have important physiological properties, and it was with this object in view that the study of the condensation of aniline with boric acid was undertaken. From the stable boranilide which was obtained, a series of derivatives has been prepared.

Ditte (*Compt. rend.*, 1887, **105**, 813) prepared aniline borate,  $\text{NH}_2\text{Ph}_2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , and Schiff (*Annalen, Suppl.*, 1867, **5**, 209) describes an "anilide of boric acid," prepared from ethyl borate and aniline, as being readily decomposed by water. It would appear that Schiff's compound was identical with that prepared by Ditte.

In the present work a mixture of molecular quantities of boric acid and aniline was heated at 135—140° with the addition of a small quantity of zinc chloride as condensing agent. Aniline does not, however, condense with orthoboric acid owing to the fact that at 100° orthoboric acid is converted into metaboric acid with the elimination of one molecule of water; so that condensation at the above temperature really takes place between aniline and metaboric acid.

As the condensation-products are very stable, it would appear that the nitrogen atom is directly linked with boron and not with oxygen; in the latter event the compounds would have been more easily hydrolysed than was found to be the case.

In the compounds described in this paper, the presence of the boric acid residue was detected in each case.

The well-known glycerol method for the quantitative estimation of boric acid (produced by decomposing the compounds with sulphuric acid with or without the addition of potassium dichromate) did not give satisfactory results. The estimation of carbon, although carefully carried out, was vitiated by the absorption of some volatile boric acid in the potash bulbs. The determination of the molecular weight of boranilide by analysis of the platinichloride as well as the estimation of nitrogen by Dumas' method conclusively show, however, that the condensation takes place between molecular quantities of boric acid and aniline, as stated above.

Boranilide satisfactorily responds to Tafel's colour reaction for anilides (*Ber.*, 1892, **25**, 412).

The constitution of boranilide,  $C_6H_5NH \cdot BO$ , is supported by the fact that it yields nitroso- and other derivatives exactly as would be expected. It appears, therefore, that the anilide, both in the free state and in acid solution, has the above constitution, whilst when dissolved in alkali hydroxide solution it has the tautomeric formula,  $C_6H_5 \cdot N:BOH$ .

#### EXPERIMENTAL.

##### *Boranilide, $C_6H_5NH \cdot BO$ .*

A mixture of 5 grams of boric acid and 7.5 grams of aniline was heated to  $135-140^\circ$ , when 1 gram of fused zinc chloride was added and the mixture stirred. The pasty mass became solid on cooling, and was successively extracted with small quantities of water. It was then washed with very dilute hydrochloric acid, and repeatedly washed with warm water. The substance crystallised from alcohol in white needles (6.5 grams), which did not melt at  $212^\circ$  (Found: N = 11.32; M.W. (from platinichloride) = 119.7.  $C_6H_5ONB$  requires N = 11.76 per cent. M.W. = 119.0).

Boranilide dissolves in acids or alkali hydroxides. The *hydrochloride* forms thin, green plates decomposing at  $108-110^\circ$  (Found: Cl = 22.40.  $C_6H_5ONB \cdot HCl$  requires Cl = 22.82 per cent.). The *platinichloride* forms small, yellow crystals which gradually become green (Found: Pt = 30.28.  $(C_6H_5ONB)_2H_2PtCl_6$  requires Pt = 30.09 per cent.).

##### *Benzoylboranilide, $C_6H_5NBz \cdot BO$ .*

This was prepared by adding benzoyl chloride to a solution of boranilide in glacial acetic acid or by adding aqueous potassium

hydroxide to a solution of boranilide (6 grams) in benzoyl chloride (7 grams). The product is a white powder which melts at 166° (Found: C=69.59; H=4.87.  $C_{13}H_{10}O_2NB$  requires C=69.95; H=4.48 per cent.).

*Thioboranilide*,  $C_6H_5NH\cdot BS$ .

A mixture of boranilide and excess of flowers of sulphur was heated until the sulphur melted, when the anilide dissolved in it. The heating was continued for ten minutes. In another preparation boranilide was heated with phosphorus pentasulphide. In each case a hard solid was produced, which was powdered and repeatedly washed with warm carbon disulphide. A yellowish-grey powder was obtained, having a faint odour of mercaptan. It is insoluble in water, alcohol or ether, but soluble in acids, and melts at 109–110° (Found: N=9.91.  $C_6H_6NSB$  requires N=10.37 per cent.).

*Nitroboranilide*,  $C_6H_5N(NO)\cdot BO$ .

Boranilide was dissolved in excess of hydrochloric acid and a solution of sodium nitrite added. A reddish-yellow oil was produced which solidified after some time to a brownish-pink solid. On adding alcohol to the oil it readily solidifies in plates melting at 83°. The substance dissolves in ether, and the ethereal solution responds to Liebermann's reaction (Found: N=18.22.  $C_6H_5O_2N_2B$  requires N=18.91 per cent.).

*Bromoboranilide*,  $C_6H_5Br\cdot NH\cdot BO$ .

Of the three bromoboranilides which have been prepared, that having the highest melting point is assumed to be the para-, that with the lowest the ortho-, and the remaining one the meta-isomeride.

*p-Bromoboranilide*.

Bromine was added to an acetic acid solution of boranilide and the precipitate was shaken with chloroform: a white powder remained which consisted of an acetate soluble in water. On warming the aqueous solution with potassium carbonate solution, the free compound, melting at 121–122°, was obtained (Found: Br=39.86.  $C_6H_5ONBrB$  requires Br=40.41 per cent.).

*o-Bromoboranilide.*

On evaporating the chloroform solution obtained in the preceding experiment a pale pink powder was obtained, the aqueous solution of which, when warmed with potassium carbonate, gave a very pale yellow substance melting at  $82^\circ$  (Found: Br=40.14.  $C_6H_5ONBrB$  requires Br=40.44 per cent.).

*m-Bromoboranilide.*

This was prepared by the action of a sulphuric acid solution of bromine on a solution of boranilide in sulphuric acid. Almost black, minute crystals separated, the aqueous solution of which, when boiled with potassium carbonate, gave *m*-bromoboranilide as a violet powder melting at  $96-97^\circ$  (Found: Br=40.10.  $C_6H_5ONBrB$  requires Br=40.41 per cent.).

*Conversion of meta- into ortho and para Bromoboranilides.*

Without separating the almost black crystals from contact with sulphuric acid, and on boiling this *m*-bromo derivative for a short time with water, a sudden change takes place and the black substance is converted into a pale pink powder. This is gently warmed with chloroform, when a white substance remains which dissolves in water. The aqueous solution, when boiled with potassium carbonate solution, yields a compound (m. p. 120-122°) which is evidently *p*-bromoboranilide, whilst the chloroform solution, on evaporation, gives a substance from which, when boiled with potassium carbonate, a pink powder (m. p. 83-84°) is produced, evidently the *o*-bromo derivative.

*Benzoyl-p-bromoboranilide,  $C_6H_5Br \cdot NBz \cdot BO$ .*

Benzoyl chloride was gradually added to a solution of *p*-bromoboranilide in glacial acetic acid, when the solution became turbid. On shaking and allowing to remain, microscopic, white, cubic crystals separated, melting at  $128-130^\circ$  (Found: Br=25.82.  $C_{13}H_7O_2NBrB$  requires Br=26.51 per cent.).

*Boryldiazoaminobenzene,  $C_6H_5 \cdot N \cdot N \cdot NPh \cdot BO$ .*

To 5 grams of nitrosoboranilide 3 grams of aniline were added, and then a mixture of hydrochloric acid, alcohol, and ether. On boiling, no action apparently took place, but on adding water and boiling the solution became red and a heavy oil separated, which

on cooling and shaking, soon solidified to crystalline, red plates melting at 109°.

Above 130° the compound suddenly decomposes with a feeble explosion. During combustion by Dumas' method the burners below the mixture of the substance and copper oxide, as well as a little in front of and behind it, were kept very low. In spite of his precaution a low result for nitrogen was obtained owing to the rather sudden evolution, and consequently incomplete reduction, of the oxides of nitrogen (Found: N=18.13.  $C_{12}H_{10}ON_3B$  requires N=19.29 per cent.).

*Borylhydrazoaminobenzene*,  $C_6H_5\cdot NH\cdot NH\cdot NPh\cdot BO$ .

On adding stannous chloride and hydrochloric acid or zinc and hydrochloric acid to the red alcoholic solution of boryldiazoaminobenzene, the red solution soon became colourless, and the hydrazo-compound was isolated by rendering the solution alkaline and extracting with ether. It melts at 123—124°, dissolves in hydrochloric acid, and gives a yellow nitroso-derivative, which responds to Liebermann's reaction.

*Boro- $\alpha$ -phenyl- $\beta$ -aminophenylhydrazide*,  
 $NH_2C_6H_4NH\cdot NPh\cdot BO$ .

A solution of 4 grams of the above hydrazo-compound was boiled with concentrated hydrochloric acid, and the hydrochloride basified with ammonia. The greyish-yellow base (3.4 grams) is soluble in alcohol and melts at 163—166° (Found: N=17.97.  $C_{12}H_{12}ON_3B$  requires N=18.66 per cent.).

*Boro- $\alpha$ -phenylhydrazido-benzenazophenol*,  
 $OH\cdot C_6H_4\cdot NN\cdot C_6H_4\cdot NH\cdot NPh\cdot BO$ .

Four grams of the above base were diazotised and combined with 2 grams of phenol in alkaline solution. The brown product (3.4 grams) is sparingly soluble in cold water, more readily so in alcohol, and dissolves readily in acids or alkali hydroxides. It melts at 152—153° to a deep violet liquid.

The hydrochloride crystallises in dark brown needles.

The dibenzoyl derivative,  $OBz\cdot C_6H_4\cdot NN\cdot C_6H_4\cdot NBz\cdot NPh\cdot BO$ , prepared from 5 grams of the azo-compound by the Schotten-Baumann reaction (yield, 8.2 grams), is a pale brown substance insoluble in water, sparingly soluble in alcohol, but readily so in ether, from which it separates in needles melting at 113—115°.

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CXXII.—*The Ethylene-Oxide Structure of Sucrose and some Other Carbohydrates.*

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The structural formula of sucrose has long been a subject of research; the more recent work of Haworth and Law (T., 1916, 109, 1314) has afforded evidence that it is formed by the fusion of a molecule of  $\alpha$ -glucose having the butylene-oxide structure and of  $\alpha$ -fructose having the ethylene-oxide structure. When hydrolysed in presence of acids, these forms are the first to be produced, but subsequently they undergo, more or less rapidly, isomeric changes, forming, first, the corresponding butylene-oxide form of fructose and then the mixture of  $\alpha$ - and  $\beta$ -modifications of this in equilibrium, and, secondly, the  $\beta$ -butylene-oxide form of glucose, as well as small quantities of the corresponding ethylene-oxide forms. The final mixture, which has the well-known optical rotatory power and other physical characteristics of invert-sugar, is thus a very complex mixture of substances, and there is little wonder that its crystallising power is low and that its nature is hard to establish.

Haworth and Law's proof of the presence of the ethylene-oxide form of fructose in sucrose is based on the complete methylation of the disaccharide and the identification of the methyl fructose formed after hydrolysis.

In a recent communication (T., 1919, 115, 1410) we have adduced evidence of the existence in small proportions of an ethylene-oxide modification of glucose, fructose, etc., in presence of acid, and shown how the reduction of permanganate affords an indication of the amount of this form present. It appeared of interest, therefore, to use this method to detect the initial liberation of the ethylene-oxide form of fructose from sucrose, and so confirm the observations of Haworth and Law.

The quickest and most delicate method of hydrolysing sucrose is by means of invertase, and as the action is in neutral solution, the subsequent isomeric changes are relatively slow. The figures quoted in table I show a rapid increase in the reducing power to permanganate, and indicate conclusively the presence of what we consider to be the ethylene-oxide form of fructose, since the butylene-oxide form is relatively stable to permanganate.

When sucrose is hydrolysed in presence of hydrochloric acid, action is slower, and isomeric change is promoted by the acid. The figures in table II give very little indication of the presence of any more of the ethylene-oxide form than is normally produced by acid of this strength in a mixture of glucose and fructose, and presumably the ethylene-oxide form first produced had undergone rapid rearrangement into the butylene-oxide form in presence of the acid.

Anomalous results have been obtained, however, if the mixture of sugar and acid is neutralised before the addition of permanganate. These solutions appear to be approximately twice as sensitive to permanganate, and we are inclined to attribute this to some as yet unexplained disturbing factor other than the persistence of an excess of the ethylene oxide form. It may be recalled that we observed that an acid solution of glucose or fructose, if neutralised simultaneously with the addition of permanganate, gave reduction times almost identical with those of the acid solution, and we considered that this indicated the persistence of the active form of the sugar after neutralisation of the acid had taken place.

In our previous communication we drew attention to the relative activities of glucose, mannose, and fructose towards permanganate, both in acid and in alkaline solution. We have now made similar experiments with galactose, arabinose, and xylose. The comparative times of reduction of the standard quantity of permanganate by acid and alkaline solutions of these sugars, and by the respective solutions when neutralised simultaneously with the addition of permanganate, are:

Age of Solution :-	N 10-HCl.				N 18-NaOH.			
	Fresh.		Five hours.		Fresh.		Five hours.	
	Acid.	Neutd.	Acid.	Neutd.	Alk.	Neutd.	Alk.	Neutd.
Glucose	29.0	27	29.0	28	11	180	3.0	48
Mannose	13.0	12	12.0	12	25	90	9.0	46
Fructose	17.0	15	16.0	18	3	60	1.25	11
Galactose	8.0	12	5.5	21	26	26	3.5	Indef.
Arabinose	2.5	11	2.5	11	31	38	1.5	75
Xylose	4.0	20	6.0	18	18	32	1.5	75

With the single exception of mannose, there is relatively little difference between the sugars in their behaviour in alkaline solution, and it would appear that the configuration of the rest of the molecule has but little effect on the readiness to undergo enolisation.

In acid solution the differences are more marked, the pentoses being especially active as reducing agents: there is no very apparent connexion between activity and configuration.

The proof of the existence of ethylene-oxide forms of the simple sugars has introduced a new conception into the structural chemistry of the carbohydrates which may have far-reaching significance. In consequence, until further experimental evidence has been accumulated, it is advisable to exercise caution in the interpretation of differences between the various sugars such as we have just recorded. As it may be some time before we can return to this investigation, we wish to place the facts on record for the benefit of other workers in this field.

#### EXPERIMENTAL.

##### *Hydrolysis of Sucrose by Invertase.*

A quantity of pressed yeast was autolysed in the presence of toluene for some days, and the aqueous filtrates were precipitated by excess of alcohol; the invertase was collected, redissolved in a little water, and again precipitated by alcohol. The filtered product was dissolved in water and the solution divided into three equal portions: two of these were employed in the hydrolysis of 250 c.c. of  $M/36$ - and  $5M/36$ -solutions of sucrose (giving total hexose concentrations of  $M/18$  and  $5M/18$ , as in our former work), whilst the third was made up to 250 c.c. with pure water.

The solutions were maintained at  $25^\circ$ , and 10 c.c. portions were tested from time to time with 2 c.c. of  $N/100$ -permanganate; the colour changes were not the same as with acid solutions, but two fairly definite tints were observable, namely, a clear brown immediately after the last trace of pink had faded, and, finally, a very clear pale yellow.

The solution of invertase in water alone was tested with the others, and it was found that reduction of the permanganate was very slow, the clear brown only being reached after seventy to ninety minutes, whilst the further change to pale yellow occupied many hours.

An attempt was made to examine the effect of introducing

*N*/10-hydrochloric acid on the permanganate test, but it appeared that in presence of acid the invertase alone acquired the power of very rapidly reducing permanganate.

Table I illustrates the results obtained with invertase in neutral solutions of *M*/36- and 5*M*/36-sucrose, with the corresponding optical rotatory power of the solutions.

TABLE I.

Age of solution (hours).	<i>M</i> /36-Solution.			5 <i>M</i> /36-Solution.		
	Permanganate test.		[ $\alpha_D$ ].	Permanganate test.		[ $\alpha_D$ ].
	Brown. (minutes.)	Yellow. (minutes.)		Brown. (minutes.)	Yellow. (minutes.)	
0.0	45	100	+ 61.5°	30	100	+ 63.3°
0.5	35	53	41.7	15	28	54.7
1.0	25	35	28.3	10	22	45.7
1.5	22	35	20.0	8	18	38.3
2.5	20	30	—	8	19	—
3.0	19	25	—	8	15	—
3.5	19	26	1.7	7	14	12.3
4.5	20	25	10.0	7	11	2.7
5.5	20	25	18.3	6	9	— 8.0
10.3	20	25	20.0	6	9	18.0
24.0	20	25	21.5	6	9	21.0

#### *Hydrolysis of Sucrose by N/10-Hydrochloric Acid.*

TABLE II.

Age of solution (hours).	<i>M</i> /36-Solution.			5 <i>M</i> /36-Solution.		
	Permanganate test.		[ $\alpha_D$ ].	Permanganate test.		[ $\alpha_D$ ].
	Acid. (minutes.)	Neutd. (minutes.)		Acid. (minutes.)	Neutd. (minutes.)	
0.0	230*	110*	142	57	+ 62.8°	
1.0	155	40*	120	30	59.0	
3.0	115	36*	60	27	—	
5.0	100	16†	49	23	49.0	
23.7	35	27	19	17	32.3	
30.0	—	—	16	10	24.0	
72.3	31	17	18	10	4.0	

\* Indefinite end-point.

† Precipitation set in.

#### *Mean Comparative Figures for Fructose and Glucose.*

The following are the mean times of reduction of permanganate, in the acid and neutralised tests, found in the former work for solutions of fructose and glucose in *N*/10-hydrochloric acid:

	Calculated		mean of		<i>M/36-Fructose +</i>
	<i>M/18-Fructose</i> (found).	<i>M/18-Glucose</i> (found).	<i>M/18-fructose</i> and <i>M/18-glucose</i> .	<i>M/36-Glucose</i> (found).	
Acid .....	16.5	29.2	22.9	22.8	
Neutralised	17.0	28.0	22.3	26.8	
	Calculated mean of		<i>5M/18-fructose and</i> <i>5M/18-glucose.</i>		
	<i>5M/18-Fructose</i> (found).	<i>5M/18-Glucose</i> (found).	<i>5M/18-fructose and</i> <i>5M/18-glucose.</i>		
Acid .....	7.7	19.4	13.6		
Neutralised ...	7.8	19.0	13.4		

[Received, August 2nd, 1920.]

### CXXIII.—*Triethylene Tri- and Tetra-sulphides.*

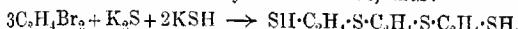
By Sir PRAFULLA CHANDRA RÂY.

In the preparation of ethylene mercaptan by the interaction of ethylene dibromide and alcoholic potassium hydrogen sulphide, after removal of alcohol and ethylene mercaptan by steam distillation, continued passage of steam furnishes a milky distillate solidifying to a crystalline mass, which, when recrystallised from hot alcohol, melts at 113°, and consists of *triethylene trisulphide*,  $(C_2H_4)_3S_3$ . The non-volatile oil remaining in the distilling flask also solidified on cooling to a crystalline mass, consisting of a mixture of three polymeric *triethylene tetrasulphides*. By extraction with alcohol, the  $\alpha$ -modification (m. p. 76°) was obtained; the remainder, on extraction with benzene, gave the  $\beta$ -modification (m. p. 102—104°), and the insoluble residue furnished the  $\gamma$ -modification (m. p. 116°). The alkaline liquid which remained behind in the flask yielded, on acidification, an oil, which has been proved to be *triethylene disulphide dimercaptan*,  $(C_2H_4)_3S_2(SH)_2$ . On treatment with mercuric chloride, it gave the corresponding *chloromercaptide*,  $(C_2H_4)_3S_2(SHgCl)_2$ . This dimercaptan, when treated in ethereal solution with an alcoholic solution of iodine, gives the  $\beta$ -tetrasulphide (m. p. 191°), and its methyl-alcoholic solution slowly oxidises in the air to  $\delta$ -*triethylene tetrasulphide* (m. p. 59—60°). The molecular weight of this variety was found to be 816, which corresponds with four times the formula,  $(C_2H_4)_3S_4$ . The  $\beta$ -modification is sparingly soluble in boiling benzene or chloroform, and its molecular weight could not be

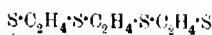
determined with exactness, but evidence pointed to its having a much higher molecular weight, indicating that in this case there was a coalescence of more than four simple molecules. In boiling chloroform, the substance undergoes partial slow spontaneous polymerisation, as was proved by the fact that successive crops differed in melting point and were only sparingly soluble in benzene. The insoluble portion melted at about 114°.

It seems probable that the  $\gamma$ -modification, which is insoluble in ordinary solvents, has a much higher molecular weight.

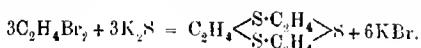
The formation of the compounds may be explained according to the following scheme. The alcoholic solution of potassium hydroxide, on being saturated with hydrogen sulphide, contains potassium sulphide in addition to potassium hydrogen sulphide, and this mixture acts on ethylene dihydrogen, thus:



Evidently, the tetrasulphides are the products of spontaneous aerial oxidation of the dimercaptan, thus:



The formation of the trisulphide may be explained thus:



#### EXPERIMENTAL.

The method of preparation (from 100 grams of ethylene dihydrogen) was exactly as described by Fastender (*Ber.*, 1887, **20**, 161). After removal of alcohol and ethylene mercaptan by means of steam, there separated from the distillate a solid, which was pressed on porous plate (1.29 grams) and crystallised from alcohol, when it melted at 113°, and consisted of *triethylene trisulphide* (Found\*: C=37.84; H=6.80; S=53.06, 53.54.  $\text{C}_6\text{H}_{12}\text{S}_3$  requires C=40.00; H=6.67; S= 53.33 per cent.).

The non-volatile oil, which solidified on cooling (6.5 grams), was

\* As these compounds are very rich in sulphur, the length of the lead chromate in the combustion tube was much increased so as to preclude the possibility of sulphur dioxide escaping absorption. Moreover, in some cases the alkali hydroxide in the potash bulb, after analysis, was oxidised with bromine, warmed and acidified with hydrochloric acid and treated with barium chloride, but no barium sulphate could be detected.

In the estimation of sulphur, Carius' method was adopted by which the compound was converted into the sulphonie acid. The acids were neutralised with sodium carbonate, evaporated to dryness, and then fused with potassium nitrate so as to transform the sulphonate into sulphate.

extracted completely with hot alcohol, the solution furnishing crystals of  $\alpha$ -triethylene tetrasulphide melting at 75° (Found: C=33.88; H=7.42.  $C_6H_{12}S_4$  requires C=33.96; H=5.66 per cent.).

The residue was then similarly treated with boiling benzene, which extracted  $\beta$ -triethylene tetrasulphide melting at 102—104° (Found: C=33.92; H=6.94.  $C_6H_{12}S_4$  requires C=33.96; H=5.66 per cent.).

The final insoluble portion consisted of  $\gamma$ -triethylene tetrasulphide melting at 116° (Found: C=34.30, 33.59; H=6.41, 7.90; S=59.07.  $C_6H_{12}S_4$  requires C=33.96; H=5.66; S=60.38 per cent.).

The alkaline liquid, on acidification, gave an oil, which was extracted with ether (8.5 grams), and consisted of triethylene disulphide dimercaptan boiling at 260—263° (Found: S=60.86.  $C_6H_{14}S_4$  requires S=59.80 per cent.).

Its methyl-alcoholic solution, on exposure to air, gave  $\delta$ -triethylene tetrasulphide melting at 59—60° (Found: C=33.05; H=6.29; S=60.55. M.W. by osmotic method in chloroform=815.5, 815.8.  $C_{24}H_{48}S_{16}$  requires C=33.96; H=5.66; S=60.38 per cent. M.W.=848).

On treatment with mercuric chloride, it gave the dichloro-mercaptide (Found: C=10.34; H=2.22; Cl=9.40, 10.81; S=18.54; Hg=58.44.  $C_6H_{12}Cl_2S_2Hg_2$  requires C=10.54; H=1.75; Cl=10.40; S=18.74; Hg=58.57 per cent.).

Various derivatives of the above polysulphides are in course of preparation.

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## Organic Chemistry.

**The Origin of Petroleum. Formation from Free Fatty Acids or Soaps. Formation from Animal Hydrocarbons.** AD. GRÄF and TH. WIRTH (*Ber.*, 1920, **53**, [B], 1301—1312).—A modification of Engler's theory of the origin of petroleum from fats has recently been put forward by Pictet and Potok (A., 1919, i, 569), who base their ideas on the experimental results obtained by the distillation of sodium stearate and sodium oleate under diminished pressure, whereby they claim to have isolated hydrocarbons of high molecular weight. The authors have attempted to repeat Pictet and Potok's experiments as far as is possible from the description given in the literature, and have obtained totally different results. Paraffins of high molecular weight are not obtained; the main products are liquid unsaturated hydrocarbons and pentatriacontanone, the latter of which is practically completely decomposed when the distillates are fractionated at the ordinary pressure.

The recent isolation of hydrocarbons by Mastbaum, Tsujimoto, and Chapman in considerable quantity from the liver oils of certain fish may possibly have an important bearing on the origin of petroleum. In favour of this hypothesis, it may be noted that these fish are most closely allied to those of past ages, that the animal hydrocarbons with branched chains contain asymmetric carbon atoms which may account for the optical activity of petroleum, and lastly that the conversion of complex hydrocarbons into naphthalenes can be readily explained, since, for example, Chapman has found that spinacene yields a cyclic hydrocarbon when distilled over sodium.

H. W.

**Pyrogenic Acetylene Condensations. VI.** RICHARD MEYER and KURT TAEGER (*Ber.*, 1920, **53**, [B], 1261—1265).—Further examination of the mixture of picrates obtained from the fractions of higher boiling point derived from the acetylene tar described previously (A., 1919, i, 72) has shown the presence of fluorene, naphthalene, anthracene, phenanthrene, pyrene, small quantities of fluoranthene, and a hydrocarbon,  $C_{17}H_{16}$ , m. p. 186°, which yields a picrate, m. p. 231°.

H. W.

**Catalytic Oxidation of Alcohols by the Use of Metallic Oxides and of Finely Divided Metals.** J. B. SENDERENS (*Ann. chim.*, 1920, [ix], **13**, 266—283).—The oxidation of alcohols under the catalytic influence of various powdered metallic oxides (nickel, copper, vanadium, molybdenum, zinc oxides) gave unsatisfactory results in so far as the production of aldehydes or acids is concerned.

Various metals were tried in the form of turnings or powder as  
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catalysts for this oxidation, but the only one which gave at all satisfactory results was silver. W. G.

**The Phosphatides.** ERNEST FOURNEAU (*Bull. Soc. chim. Biol.*, 1920, **2**, 67-87).—A general discussion of these substances. It appears certain that ordinary "lecithin" is a mixture of true lecithin and cephalin. J. C. D.

**Density and Coefficient of Expansion of  $\beta\beta'$ -Dichloro-diethyl Sulphide.** JOHN A. WILKINSON and CHRIS WERNLUND (*J. Amer. Chem. Soc.*, 1920, **42**, 1382-1385).—The density and coefficient of expansion of dichlorodiethyl sulphide have been determined by the dilatometric method at temperatures between 15° and 90°. The density changes uniformly from 1.2790 at 15° to 1.1996 at 90°, the change being 0.001058 per degree. The coefficient of expansion is also uniform over this temperature range, and amounts to 0.000881 c.c. per degree. J. F. S.

**Synthetic Notes [Alkyl Sulphuryl Chlorides.  $\alpha$ -Bromo- $\alpha$ -phenylacetonitrile.  $\alpha$ -Bromo- $\alpha$ -oximinoacetone and  $\alpha\alpha$ -Dichloro- $\alpha$ -nitrosoethane].** WILHELM STEINKOPF, WALTER MIEG, and JULIUS HEROLD (*Ber.*, 1920, **53**, [B], 1144-1148).—The methods of preparation (in part new and in part modifications of older processes) of various substances used by the authors in recent work are described.

*n*-*Propylsulphuryl chloride*,  $\text{OPr}\cdot\text{SO}_2\text{Cl}$ , b. p. 70-72°/20 mm. (slight decomp.), was on one occasion obtained by the action of sulphuryl chloride on *n*-propyl alcohol; attempts to repeat the preparation from other specimens of the reagents failed for some unexplained reason. *iso*Propyl and *iso*amyl alcohols are converted by sulphuryl chloride into the corresponding *sulphuryl chloride*, but these cannot be distilled, and gradually decompose when preserved at the ordinary temperature. Ethylene chloro- and bromo-hydribs are almost quantitatively transformed by sulphuryl chloride into *ω*-chloroethylsulphuryl chloride,  $\text{SO}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , b. p. 89-91°/water-pump vacuum, and *ω*-bromoethylsulphuryl chloride, b. p. 100-105°/18 mm., respectively. Hydrogen chloride is evolved when sulphuryl chloride acts on ethyl glycolate, glycol monoacetate, and ethyl or methyl lactate, but the other products decompose when distilled or preserved at the ordinary temperature. Methylsulphuryl bromide could not be obtained from the corresponding chloride and hydrogen bromide, or from sodium methyl-sulphate and phosphorus pentabromide, or phosphorus and bromine. Methylsulphuryl chloride and potassium thiocyanate in acetone solution yield methyl thiocyanate,  $\text{SO}_2\text{Cl}\cdot\text{OMe} + \text{KCNS} = \text{MeSCN} + \text{SO}_2\text{Cl}\cdot\text{OK}$ . Phenol is exclusively chlorinated by sulphuryl chloride, yielding *o*-chlorophenol and, possibly, 2:4-dichlorophenol. The product obtained from phosphorus pentachloride and potassium phenyl sulphate has b. p. 143-145°/45 mm., and appears to be phenylphosphoryl dichloride,  $\text{OPh}\cdot\text{POCl}_2$ .

Phenylbromoacetonitrile is obtained as a yellow oil, b. p. 132—134°/12 mm., by the action of bromine vapour on phenylacetonitrile at 105° under the influence of powerful light. Tribromoacetyl bromide, b. p. 88—90°/12 mm., 210—215°/atmospheric pressure, is conveniently prepared from tribromoacetic acid and phosphorus tribromide.

Improved methods are given for the isolation of  $\alpha$ -bromo- $\alpha$ -oximinoacetone,  $\text{COMe} \cdot \text{CBr} \cdot \text{N} \cdot \text{OH}$ , m. p. 123—125°, and of  $\alpha\alpha$ -dichloro- $\alpha$ -nitrosoethane,  $\text{CH}_3 \cdot \text{CCl}_2 \cdot \text{NO}$ , b. p. 67—69°. H. W.

**The Chloro-derivatives of Methyl Formate and Methyl Carbonate.** V. GRIGNARD, G. RIVAT, and ED. URHAIN (*Ann. chim.*, 1920, [ix], 13, 229—265).—A full account of work already published (this vol., i, 138, 139). W. G.

**The Successive Stages of the Hydrolysis of Triacetin.** EIICHI YAMASAKI (*J. Amer. Chem. Soc.*, 1920, 42, 1455—1468).—It is shown that triacetin conforms to the statement that the hydrolysis of an ester formed by a polyhydric alcohol and a monobasic acid takes place according to the simple rule that each ester radicle has an equal rate of hydrolysis. Thus their rates are simply expressed in the same way as those of the successive reactions  $M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow M_4$ , which have, respectively, the velocity constants  $3k$ ,  $2k$ ,  $k$ .  $M_1$  represents the triacetin,  $M_2$  the two isomeric diacetins,  $M_3$  the two isomeric monoacetins, and  $M_4$  glycerol. Detailed results of the hydrolysis of triacetin in 0.961*N*-hydrochloric acid at 35° are given. W. G.

**Chemical Nature of Margosic Acids (Fatty Acids of the Nim or Margosa Oil). Recent Conclusions Drawn from Experimental and Clinical Use of (Metallic) Margosates and Ethyl Margosate.** K. K. CHATTERJEE (*Indian Med. Gaz.*, 1919, 54, 171—174).—The characteristic acid of this oil belongs to the linolic series, and is named *margosic acid* by the author, who suggests  $\text{C}_{22}\text{H}_{40}\text{O}_2$  for its formula. It forms about 23% of the total fatty acid present in nim oil. It is liquid at the ordinary temperature, yellow, and is optically inactive. Its sodium and potassium salts are soluble in water; its lead and barium salts are soluble in ether and light petroleum. The zinc, calcium, bismuth, mercury, and silver salts were also prepared. Ethyl margosate, prepared from the mixed fatty acids in this oil, is a clear, reddish-brown liquid having a fruity odour and a high b. p., and is more readily hydrolysed than potassium margosate. One c.c. of it injected intravenously gives rise to no harmful symptoms (in man). Post-mortem findings in a rabbit killed by injecting this compound showed that death was due to asphyxia. The author has treated several cases of leprosy, syphilis, and skin diseases by injecting the ester, sodium, and potassium salts of this acid with marked success.

CHEMICAL ABSTRACTS.

“ “ ”

**Bromination of Glutaconic Acid and its Diethyl Ester.** P. E. VERKADE and J. Coops, jun. (*Rec. trav. chim.*, 1920, **39**, 586—593).—By exposing dry powdered glutaconic acid in a thin layer to the action of bromine vapour for seventy-two hours, the authors have obtained  $\alpha\beta$ -dibromoglutaric acid, m. p. 157°, without the formation of any hydrogen bromide. This acid, when debrominated by means of zinc and dilute sulphuric acid, gave only glutaconic acid. The authors consider that the  $\alpha\beta$ -dibromoglutaric acid obtained is the *trans*-form.

When ethyl glutaconate was brominated, even with the utmost precautions, there was always some hydrogen bromide formed. The ester obtained was not pure, but was in all probability the  $\alpha\beta$ -dibromoglutarate. When debrominated, the only product it yielded was glutaconic acid.

W. G.

**Relations between the Configuration and the Optical Rotatory Power of some Derivatives of Acids of the Sugar Group.** (MLE) Th. W. J. VAN MARLE (*Rec. trav. chim.*, 1920, **39**, 549—572).—With the view of seeing whether Hudson's rule (A., 1917, i, 318), as to the relationship between the direction of rotation and the configuration of the phenylhydrazides of the mono-basic acids of the sugar groups, is applicable to other derivatives of such acids, the author has prepared a number of derivatives described below.

*d*-Glueconic acid gives a hydrazide, m. p. 142°,  $[\alpha]_D^{25} + 30.4^\circ$  (in water),  $[\alpha]_D^{25} + 20.9^\circ$  (in pyridine), yielding a benzylidene derivative, m. p. 157°,  $[\alpha]_D^{25} + 48.6^\circ$  (in pyridine), and a p-methoxybenzylidene derivative, m. p. 185°,  $[\alpha]_D^{25} + 54.0^\circ$  (in pyridine); a p-bromophenyl-hydrazide, m. p. 203°,  $[\alpha]_D^{25} + 3.6^\circ$  (in water),  $[\alpha]_D^{25} - 15.3^\circ$  (in pyridine); a *p*-tolylhydrazide, m. p. 201°,  $[\alpha]_D^{25} + 5.0^\circ$  (in water),  $[\alpha]_D^{25} + 2.0^\circ$  (in pyridine); an *o*-tolylhydrazide, m. p. 218°,  $[\alpha]_D^{25} + 13.7^\circ$  (in water),  $[\alpha]_D^{25} + 5.1^\circ$  (in pyridine); a *m*-tolylhydrazide, m. p. 185°,  $[\alpha]_D^{25} + 4.5^\circ$  (in water),  $[\alpha]_D^{25} + 2.7^\circ$  (in pyridine); an anilide, m. p. 171°,  $[\alpha]_D^{25} + 50.6^\circ$  (in water); a *p*-toluidide, m. p. 181°,  $[\alpha]_D^{25} + 50.5^\circ$  (in water).

*d*-Mannonic acid gives a hydrazide, m. p. 161°,  $[\alpha]_D^{25} - 3.0^\circ$  (in water),  $[\alpha]_D^{25} - 38.8^\circ$  (in pyridine), yielding a benzylidene derivative, m. p. 194°,  $[\alpha]_D^{25} - 8.0^\circ$  (in pyridine), and a p-methoxybenzylidene derivative, m. p. 191°,  $[\alpha]_D^{25} - 18.8^\circ$  (in pyridine); a p-bromophenyl-hydrazide, m. p. 225°,  $[\alpha]_D^{25} - 7.3^\circ$  (in water),  $[\alpha]_D^{25} - 24.9^\circ$  (in pyridine); a *p*-tolylhydrazide, m. p. 208°,  $[\alpha]_D^{25} - 8.7^\circ$  (in water),  $[\alpha]_D^{25} - 24.8^\circ$  (in pyridine); an *o*-tolylhydrazide, m. p. 208°,  $[\alpha]_D^{25} - 10.9^\circ$  (in water),  $[\alpha]_D^{25} - 28.6^\circ$  (in pyridine), a *m*-tolylhydrazide, m. p. 214°,  $[\alpha]_D^{25} - 12.5^\circ$  (in water),  $[\alpha]_D^{25} - 24.7^\circ$  (in pyridine).

*d*-Galactonic acid gives a hydrazide, m. p. 178°,  $[\alpha]_D^{25} + 40.1^\circ$  (in water),  $[\alpha]_D^{25} + 31.1^\circ$  (in pyridine), yielding a benzylidene derivative, m. p. 193°,  $[\alpha]_D^{25} + 63.4^\circ$  (in pyridine), and a p-methoxybenzylidene derivative, m. p. 191°,  $[\alpha]_D^{25} + 67.7^\circ$  (in pyridine); a p-bromophenyl-hydrazide, m. p. 125°,  $[\alpha]_D^{25} + 2.5^\circ$  (in water),  $[\alpha]_D^{25} - 30.3^\circ$  (in pyridine);

**a** *p-tolylhydrazide*, m. p. 212°,  $[\alpha]_D^{25} + 2\cdot9^\circ$  (in water),  $[\alpha]_D^{14} - 13\cdot5^\circ$  (in pyridine); **an** *o-tolylhydrazide*, m. p. 191°,  $[\alpha]_D^{25} + 12\cdot2^\circ$  (in water),  $[\alpha]_D^{14} - 8\cdot6^\circ$  (in pyridine); **a** *m-tolylhydrazide*, m. p. 174°,  $[\alpha]_D^{25} + 0\cdot8^\circ$  (in water),  $[\alpha]_D^{14} - 15\cdot8^\circ$  (in pyridine); **an** *anilide*, m. p. 210°,  $[\alpha]_D^{25} + 62\cdot6^\circ$  (in water); **a** *p-toluidide*, m. p. 224°,  $[\alpha]_D^{25} + 72\cdot9^\circ$  (in water); **an** *o-toluidide*, m. p. 204°,  $[\alpha]_D^{25} + 49\cdot9^\circ$  (in water); **a** *m-toluidide*, m. p. 212°,  $[\alpha]_D^{25} + 63\cdot3^\circ$  (in water).

*L*-Gulonic acid gives a *hydrazide*, a syrup,  $[\alpha]_D^{25} + 4\cdot3^\circ$  (in water), yielding a *benzylidene* derivative, m. p. 173°,  $[\alpha]_D^{14} - 11\cdot2^\circ$  (in pyridine), and a *p-methoxybenzylidene* derivative, m. p. 176—177°,  $[\alpha]_D^{14} - 2\cdot9^\circ$  (in pyridine), a *p-bromophenylhydrazide*, and a *p-tolylhydrazide*, neither of which could be obtained pure.

*L*-Idonic acid gives a *hydrazide*, a syrup,  $[\alpha]_D^{25} - 21\cdot8^\circ$  (in water), yielding a *benzylidene* derivative, m. p. 153°; and a *p-tolylhydrazide*, which was not obtained pure.

*iso*-Saccharic acid gives a *hydrazide*, a syrup,  $[\alpha]_D^{25} - 11\cdot6^\circ$  (in water), yielding a *benzylidene* derivative, m. p. 147°,  $[\alpha]_D^{14} - 48\cdot2^\circ$  (in pyridine), and a *p-methoxybenzylidene* derivative, m. p. 138°,  $[\alpha]_D^{14} - 36\cdot2^\circ$  (in pyridine).

*L*-Arabonic acid gives a *hydrazide*, m. p. 138°,  $[\alpha]_D^{25} + 52\cdot6^\circ$  (in water),  $[\alpha]_D^{14} + 61\cdot8^\circ$  (in pyridine), yielding a *benzylidene* derivative, m. p. 208°,  $[\alpha]_D^{14} + 81\cdot3^\circ$  (in pyridine), and a *p-methoxybenzylidene* derivative, m. p. 208°,  $[\alpha]_D^{14} + 81\cdot7^\circ$  (in pyridine); a *p-bromophenylhydrazide*, m. p. 204° (decomp.),  $[\alpha]_D^{25} + 2\cdot4^\circ$  (in water),  $[\alpha]_D^{14} - 19\cdot0^\circ$  (in pyridine); a *p-tolylhydrazide*, m. p. 216°,  $[\alpha]_D^{25} + 4\cdot08^\circ$  (in water),  $[\alpha]_D^{14} - 3\cdot1^\circ$  (in pyridine); an *o-tolylhydrazide*, m. p. 203°,  $[\alpha]_D^{25} + 26\cdot6^\circ$  (in water),  $[\alpha]_D^{14} - 1\cdot4^\circ$  (in pyridine); a *m-tolylhydrazide*, m. p. 185° (decomp.),  $[\alpha]_D^{25} + 4\cdot6^\circ$  (in water),  $[\alpha]_D^{14} - 5\cdot0^\circ$  (in pyridine); an *anilide*, m. p. 204°,  $[\alpha]_D^{25} + 68\cdot1^\circ$  (in water); a *p-toluidide*, m. p. 200°,  $[\alpha]_D^{25} + 68\cdot2^\circ$  (in water); an *o-toluidide*, m. p. 172°,  $[\alpha]_D^{25} + 56\cdot5^\circ$  (in water), and *m-toluidide*, m. p. 186°,  $[\alpha]_D^{25} + 67\cdot7^\circ$  (in water).

*d*-Ribonic acid gives a *hydrazide*, m. p. 150°,  $[\alpha]_D^{25} + 27\cdot5^\circ$  (in water), yielding a *benzylidene* derivative, m. p. 153—155°.

*d*-Lyxonic acid gives a *hydrazide*, m. p. 188°,  $[\alpha]_D^{25} - 3\cdot6^\circ$  (in water), which yields a *benzylidene* derivative, m. p. 175° (decomp.).

The results indicate that Hudson's law (*loc. cit.*) holds equally for the hydrazides, *p*-bromophenylhydrazides, *o*-, *m*-, and *p*-tolylhydrazides, imides, anilides, and *o*-, *m*-, and *p*-toluidides, the rule being applicable for aqueous solutions, but not for solutions in pyridine. The introduction of a phenyl or tolyl radicle into the amide group results in considerable rise in the rotatory power. Of the three isomeric toluidides, the *para* invariably has the greatest rotation and the *ortho* the least.

Usually the *p*-methoxybenzylidene derivatives had a higher rotatory power than the corresponding benzylidene derivatives.

W. G.

**Ring Closure with Polycarboxylic Acids. I. The Di-anhydride of Ethanetetracarboxylic Acid.** ERNST PHILIPPI and JULIE HANUSCH (*Ber.*, 1920, **53**, [B], 1300—1301).—*Ethanetetracarboxylic anhydride*,  $O<\text{CO}-\text{CH}(\text{CO})-\text{CO}>_2\text{O}$ , colourless needles, which become discoloured at about  $150^\circ$  and decompose without melting at a higher temperature, is prepared by the action of warm acetic anhydride on ethanetetracarboxylic acid; the latter substance is re-formed by the action of water on the anhydride.

H. W.

**Improved Catalyst for the Manufacture of Acetaldehyde from Acetylene as the Primary Material, and Process for the Regeneration of the Catalyst.** SOCIÉTÉ DES ACIERIES ET FORGES DE FIRMINY (Brit. Pat. 124194).—An improved catalyst for the hydration of acetylene consists of a solution of sulphuric acid containing mercury, ferric, and vanadium salts, which, after becoming exhausted, can be regenerated by electrolytic oxidation either intermittently or continuously, using a cell with a magnetite or platinum anode and a current density of 3—5 amperes per sq. dm., the temperature being maintained at  $30$ — $40^\circ$ . By way of example, the catalyst may consist of 10—20% sulphuric acid containing in solution 2% of mercury, 0.3—0.5% of iron, and 0.025—0.1% of vanadium, the metals being present as sulphates. The optimum temperature of the bath for the conversion of acetylene into acetaldehyde is about  $65^\circ$ . G. F. M.

**The Alleged Inactivation of *d*-Mannitol.** MASTA EHRLICH (*Biochem. Zeitsch.*, 1920, **103**, 312—315).—The author confirms Grün's observation that by dissolving the alkaline earth salts in a mannitol solution, a product is obtained which shows no rotation. Unlike Grün, however, she finds that when the strontium nitrate-mannitol solution is precipitated with acetone, as described by Grün, the mannitol thus obtained is identical with the active mannitol originally used. The mannitol is therefore not inactivated by this treatment, as is alleged by Grün. S. S. Z.

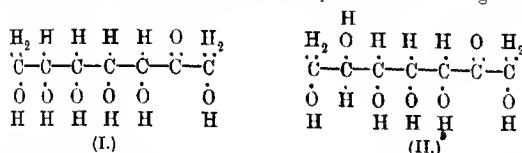
**Glucosan.** AMÉ PICTET and PIERRE CASTAN (*Compt. rend.*, 1920, **171**, 243—245).—Gélis obtained a brown, amorphous substance, which he named glucosan, by heating dextrose at  $170^\circ$  (compare *ibid.*, 1860, **51**, 331). This compound can be obtained in a pure, crystalline state if the dextrose is heated at  $150$ — $155^\circ$  under a pressure of 15 mm. So obtained, it has m. p.  $108$ — $109^\circ$ , is very deliquescent, and has  $[\alpha]_D + 69.8^\circ$  in water. It reduces Fehling's solution, and when boiled with water gives dextrose again. When dissolved in methyl alcohol saturated with ammonia, it gives a crystalline compound, which is not glucosamine or isoglucosamine. When dissolved in methyl alcohol saturated with hydrogen chloride it gives  $\alpha$ -methyl glucoside. It yields a tribenzoyl derivative and a crystalline bisulphite compound. When dissolved in methyl alcohol and mixed with a solution of sodium methoxide in the same solvent, it gives a white solum derivative, which, when

decomposed by dilute sulphuric acid, ultimately gives a methyl glucose. From its general behaviour the authors assign to glucosan the constitution  $O < \begin{array}{c} CH - CH \cdot OH \\ | \\ CH \cdot OH \cdot CH \cdot CH(OH) \cdot CH_2 \cdot OH \end{array}$ .

W. G.

**Sedoheptose, a New Sugar from Sedum Spectabile. II.** F. B. LA FORGE (*J. Biol. Chem.*, 1920, **42**, 367-374. Compare A., 1917, i, 444).— $\alpha$ -Sedoheptitol on oxidation with nitric acid gives pentahydroxypropimelic acid. Of the ten theoretically possible

heptitols, six are optically active, and of these six, five are known.  $\alpha$ -Sedoheptitol does not correspond with any of these five, and its constitution must therefore be given by the annexed formula. In the same way, considering the properties of inactive  $\beta$ -sedoheptitol and the constitution of the four possible inactive heptitols, of which only one is known, and since the  $\alpha$ - and  $\beta$ -sedoheptitols differ only in having the position of one hydroxyl group reversed, there are only two possible configurations for an  $\alpha$ -ketohexose which will give such



heptitols, namely, formulae I and II. At present it is not possible to distinguish between these two formulae.

W. G.

**Volemitol.** F. B. LA FORGE (*J. Biol. Chem.*, 1920, **42**, 375-376).— $\alpha$ -Sedoheptitol gives an acetal, m. p. 191-194°, which is identical with that from the natural heptitol, volemitol, and it is now shown that these two heptitols are identical. The m. p. for tribenzylidenevolemitol given by Bongault and Allard (A., 1903, i, 62) is erroneous.

W. G.

**Optical Properties of a Series of Heptitols.** EDGAR T. WHERRY (*J. Biol. Chem.*, 1920, **42**, 377-382).—The following are the refractive indices and densities of the eight known heptitols:

	$n_r$	$n_g$	$n_i$	D.
$\alpha$ -Mannoheptitol .....	1.538	1.545	1.549	1.485
$\beta$ -Mannoheptitol .....	1.533	?	1.545	1.470
$\alpha$ -Glucosheptitol .....	1.548	1.550	1.558	1.520
$\beta$ -Glucosheptitol .....	1.542	1.550	1.552	1.510
$\alpha$ -Sedoheptitol .....	1.550	1.555	1.562	1.520
$\beta$ -Sedoheptitol .....	1.564	1.570	1.584	1.590
$\alpha$ -Guloheptitol .....	1.554	1.560	1.570	1.560
$\beta$ -Guloheptitol .....	1.565	1.570	1.586	1.585

W. G.

**The Acidic and Basic Properties of Different Compounds.** H. I. WATERMAN and J. Groot (*Rec. trav. chim.*, 1920, **39**, 573—577).—In continuation of previous work (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, January), it is shown that the three cresols and *o*- and *m*-cresotic acids do not influence the hydrolysis of sucrose by hydrochloric acid, but that they all considerably retard the decomposition of dextrose by dilute aqueous sodium hydroxide. W. G.

**Physicochemical Investigations of the Diastatic Inversion of Sucrose.** ANDRÉE CHAUDUN (*Ann. chim.*, 1920, [ix], 13, 301—349).—A more detailed account of work already published (compare A., 1918, i, 414; ii, 357; 1919, ii, 327; this vol., ii, 24). W. G.

**Humic Acid.** F. Fuchs (*Chem. Zeit.*, 1920, **44**, 551).—Humic acid prepared from peat by the action of alkalis was found to be a true acid, and not a colloidal substance. It formed only simple salts, had a molecular weight of about 680, and contained 57·4% C, 4·6% H, and less than 1% of N and S. The salts of calcium, barium, magnesium, aluminium, copper, and iron were prepared. The silver salt was of variable composition (5 to 50% of silver). The humic acid was precipitated by both inorganic and organic acids. As stated by Albert (A., 1909, ii, 446), it dissolved as lithium humate when treated with lithium phosphate, which was decomposed in the reaction into the monohydrogen phosphate and hydroxide. Alkali humates are precipitated by sodium chloride solution, with the exception of a small residue, which can only be precipitated by acids, and when dried is soluble in sodium carbonate solution, whereas the portion precipitated by sodium chloride is much darker in colour, and when dried does not dissolve in sodium carbonate solution. On treating humic acid with sodium sulphide or sulphite, it yields a soluble sulphite compound, which reacts with aniline and other organic bases. C. A. M.

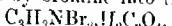
**New Derivatives of  $\beta\gamma$ -Dibromo- $\alpha$ -aminopropane and a New Base,  $C_3H_3N$ .** EMIL ABBERHALDEN and MAX PAQUIN (*Ber.*, 1920, **53**, [B], 1125—1143).—A series of products is described which originates in the spontaneous decomposition of solutions of  $\beta\gamma$ -dibromo- $\alpha$ -aminopropane in ether. In general, the constitution of the substances has not been elucidated definitely, but a preliminary account is now given.

When a solution of  $\beta\gamma$ -dibromo- $\alpha$ -aminopropane in dry ether is allowed to remain at slightly elevated temperature for two to four days, well-defined, prismatic crystals of the substance,  $C_3H_3NBr_2.HBr$ , m. p. 164°, separate. The success of the experiment depends largely on the dryness of the ether, since the presence of traces of moisture causes the separation of a yellow, amorphous substance (see later), which is only separated with great difficulty from the hydrobromide. The latter is obtained in a purer condition, m. p. 170°, from the hydrobromide of the base,

$C_6H_5NBr_2$  (see later), and is probably identical with the compound obtained in a similar manner by Paal from  $\beta$ -bromoallylamine. The free base,  $C_3H_3NBr_2$ , could not be isolated in the pure condition, since it is not volatile without decomposition, but the following salts are described: *nitrate*, pearly leaflets, m. p.  $76^\circ$  (incipient decomp.); *sulphate*,  $(C_3H_3NBr_2)_2H_2SO_4$ , crystalline powder, m. p.  $195^\circ$  (incipient decomp.); *formate*, pearly leaflets, m. p.  $105^\circ$  (slight decomp.); *oxalate*,  $C_3H_3NBr_2H_2C_2O_4$ , m. p.  $173^\circ$  (decomp.); *picrate*, yellow needles, m. p.  $169^\circ$  (slight decomp.). The base appears to be a secondary amine; it does not give the carbylamine reaction or yield a precipitate with metaphosphoric acid. It gives a *benzoyl* derivative, m. p.  $130^\circ$ , a *benzenesulphonyl* compound, m. p.  $85^\circ$ , a *monomethyl* derivative [*hydrobromide*, slender needles, m. p.  $188^\circ$  (decomp.)], and a *compound*,  $C_{10}H_7NBr_2S$ , m. p.  $161^\circ$  (incipient decomp.), with carbon disulphide. The constitution  $HC\begin{smallmatrix} < \\ \text{CBr} \end{smallmatrix} \text{NH} \begin{smallmatrix} > \\ \text{CHBr} \end{smallmatrix}$  is suggested for the base. It readily reacts with hydrogen in alcoholic solution in the presence of colloidal palladium, yielding the pure hydrobromide,  $C_3H_3NBr_2HBr$ , but the fate of the remainder of the molecule could not be established.

The yellow, amorphous substance,  $(C_3H_3NBr_2)_2$  (see above), darkens at about  $175^\circ$  and slowly melts and decomposes between  $250^\circ$  and  $260^\circ$ ; it is readily oxidised by bromine, without, however, yielding a product which is itself isolable in the pure state or yields pure salts.

An ethereal solution of the base,  $C_3H_3NBr_2$ , loses bromine when treated with sodium, and yields the base,  $C_3H_3N$ , which cannot be distilled without decomposition. Its salts with inorganic acids are extremely hygroscopic, whilst the compounds with organic acids are not generally well defined. It yields, however, an *oxalate*,  $C_3H_3N_2H_2C_2O_4$ , m. p.  $127^\circ$ , a *picrate*, needles, m. p.  $141^\circ$  (incipient decomp.), and a *compound* with mandelic acid,  $C_{10}H_7O_3N$ , m. p.  $124^\circ$ . Its close relationship to the parent base is proved by the conversion of its oxalate by bromine into the oxalate,



The constitution of the base is somewhat uncertain, since it does not give the reactions characteristic of secondary or tertiary amines, but the formula  $CH\begin{smallmatrix} < \\ \text{N} \end{smallmatrix} \begin{smallmatrix} > \\ \text{CH} \end{smallmatrix} CH$  appears most probable.

Although highly unsaturated, neither the base itself nor its salts can be hydrogenated in the presence of platinum or palladium under widely varied conditions.

Dehalogenation of the hydrobromide of the base,  $C_3H_3NBr_2$ , can be partly effected with alcoholic sodium ethoxide or with silver nitrate and nitric acid, but in this case a monobromo-derivative remains, which has not been further investigated.

When ethereal solutions of dibromoaminopropane are allowed to remain in the presence of acetone, the *substances*



m. p.  $198^{\circ}$  (decomp.), and  $C_9H_8NBr_2HBr$ , m. p.  $168^{\circ}$  (decomp.), are obtained. The former is reconverted into the hydrobromide,  $C_9H_8NBr_2HBr$ , when the ethereal solution of the liberated base is treated with bromine or simply preserved, or when the aqueous solution of the salt is acted on by excess of bromine. The *fornate*,  $C_8H_2C_3H_3NBr_2H\cdot CO_2H$ , has m. p.  $167^{\circ}$  (decomp.). The hydrobromide of the base,  $C_9H_8NBr_2$ , can be converted into an *oxalate*,  $C_6H_5NBr_2H_2C_2O_4$ , m. p.  $116^{\circ}$  (decomp.), and a *nitrate*, m. p.  $105^{\circ}$  (incipient decomp.). The hydrobromide cannot be converted by oxidative degradation into the substance,  $C_9H_8NBr_2HBr$ , nor can it be obtained from the latter or from  $C_6H_5NBr_2HBr$  by the action of acetone. An ethereal solution of the free base deposits crystals of the hydrobromide in the course of a few days. The base may be dehalogenated by the action of sodium on its ethereal solution, but the corresponding bromine-free compound is decomposed with extraordinary readiness on exposure to air; it gives characteristic *compounds* with mercuric chloride, decomposing without melting at  $100^{\circ}$ , with picric acid, darkening at  $150^{\circ}$ , but not melting below  $250^{\circ}$ , and with salicylic acid, not melting below  $350^{\circ}$ .

H. W.

**Optically Active Iridium Compounds.** A. WERNER and At. P. SITRNOFF (*Helv. Chim. Acta*, 1920, **3**, 472-486).—The authors have prepared compounds belonging to two new complex iridium series, and have succeeded in resolving them into their optically active components, confirmation being obtained of Delépine's proof that co-ordinated saturated iridium complexes possess an octahedral spacial configuration (A., 1914, i, 1048). The action of ethylenediamine on hexahalogenated compounds of quadrivalent iridium yields only dark, uncrystallisable syrups, but from ethylenediamine and complexes containing either several nitro-groups or ammonia united to a tervalent iridium atom, complexes containing two or three molecules of the diamine are readily obtained. The salts thus prepared belong to the dinitroethylenediamineiridium and the triethylenediamineiridium series, and are colourless and highly stable, those of the former series being soluble only slightly, and those of the latter about ten times as soluble. The nitro-groups of the first series are so firmly united to the metallic atom that it is necessary to heat the compounds for some hours with concentrated sulphuric acid before nitrous acid is split off; with concentrated sulphuric acid and diphenylamine, the salts of this series give, not the ordinary blue, but a bright red, coloration, which is produced by the sulphuric acid alone. The new series closely resemble, and give the same precipitation reactions as, the dinitrotetrammineiridium series (compare Werner and de Vries, A., 1909, ii, 151) and the hexammineiridium series (compare Palmaer, A., 1896, ii, 179). Although two dinitro-series are possible theoretically, only one has been obtained, and as the  $\alpha$ -camphorsulphonates are separable into their optically active components, the compounds are of the *cis*- or 1:2-dinitroethylen-

diamineiridium series; this separation is readily effected with the help of nitrocamphor. The rotatory power of the triethylene-diamine series is greater than that of the dinitro-series, and of about the same order of magnitude as those of the analogous rhodium- and platinum compounds (compare Werner, A., 1912, i, 418). In the visible part of the spectrum both series exhibit normal rotatory dispersion.

The two series of compounds were prepared by the action of ethylenediamine monohydrate on sodium dichlorotetra nitroiridate in a sealed tube at 170°, and were separated as iodides.

Salts of the racemic dinitrodiethylenediamineiridium series, 1:2-[(NO<sub>2</sub>)<sub>2</sub>Ir en<sub>2</sub>]X, the *iodide*, *bromide*, *nitrate*, *perchlorate*, and d-(*α*-*brono*)- $π$ -*camphorsulphonate*, 1:2-[(NO<sub>2</sub>)<sub>2</sub>Ir en<sub>2</sub>]d-C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>BrS, were prepared.

Salts of the *d*-dinitrodiethylenediamineiridium series: *d-camphorsulphonate*, d-[(NO<sub>2</sub>)<sub>2</sub>Ir en<sub>2</sub>]d-C<sub>10</sub>H<sub>15</sub>O<sub>4</sub>S; *bromide*, colourless, shining polyhedra, [a]<sub>D</sub> + 17.2°, [a]<sub>D</sub> + 26°, [a]<sub>E</sub> + 40°; *perchlorate*, white, crystalline powder, [a]<sub>C</sub> + 16.4°, [a]<sub>D</sub> + 24.8°, [a]<sub>E</sub> + 38.4°; *nitrate*, flat, shining needles, [a]<sub>C</sub> + 18°, [a]<sub>D</sub> + 27.2°, [a]<sub>E</sub> + 41.2°.

Salts of the *l*-dinitrodiethylenediamineiridium series: *l-camphorsulphonate*, *l*-[(NO<sub>2</sub>)<sub>2</sub>Ir en<sub>2</sub>]L-C<sub>10</sub>H<sub>15</sub>O<sub>4</sub>S; *bromide*, [a]<sub>C</sub> - 17.6°, [a]<sub>D</sub> - 26°, [a]<sub>E</sub> - 40°; *perchlorate*, [a]<sub>C</sub> - 16.8°, [a]<sub>D</sub> - 25.6°, [a]<sub>E</sub> - 39.2°; *nitrate*, [a]<sub>C</sub> - 17.6°, [a]<sub>D</sub> - 26.8°, [a]<sub>E</sub> - 41.6°.

Salts of the racemic triethylenediamineiridium series, [Ir en<sub>3</sub>]X<sub>3</sub>: *bromide* (+3H<sub>2</sub>O), *nitrate*, and *perchlorate*.

Salts of the *d*-triethylenediamineiridium series: *iodide*, [a]<sub>C</sub> + 30°, [a]<sub>D</sub> + 42°, [a]<sub>E</sub> + 56°; *nitrate*, [a]<sub>C</sub> + 41.2°, [a]<sub>D</sub> + 57.2°, [a]<sub>E</sub> + 75.2°; *perchlorate*, [a]<sub>C</sub> + 34.5°, [a]<sub>D</sub> + 48.5°, [a]<sub>E</sub> + 64°.

Salts of the *l*-triethylenediamineiridium series: *d-camphornitronate*, [Ir en<sub>3</sub>](d-C<sub>10</sub>H<sub>15</sub>O<sub>4</sub>N)<sub>3</sub>; *bromide*, (+2H<sub>2</sub>O), [a]<sub>C</sub> - 36°, [a]<sub>D</sub> - 50°, [a]<sub>E</sub> - 66.5°; *nitrate*, [a]<sub>C</sub> - 41.5°, [a]<sub>D</sub> - 57.5°, [a]<sub>E</sub> - 76°; *perchlorate*, [a]<sub>C</sub> - 34°, [a]<sub>D</sub> - 47.5°, [a]<sub>E</sub> - 63°.

T. H. P.

**Attempts to Prepare Derivatives of Diaminoacetylene.** PAUL RUGGELI (*Helv. Chim. Acta*, 1920, **3**, 559—572. Compare A., 1917, i, 22).—With the object of obtaining derivatives of diaminoacetylene, those methods of decomposition which usually yield amines with one carbon atom less than the original compounds have been applied to acetylenedicarboxylic, dibromomaleic, and dibromofumaric acids. The only method giving promising results is that in which the hydrazide and azide form intermediate steps; with dibromomaleic acid hydrazine forms a closed ring hydrazide, with dibromofumaric acid degradation occurs in the desired direction, but has not as yet been carried sufficiently far. Unlike imidazole itself, tribromoimidazole yields no ethylene derivative, but merely a benzoyl compound when treated with benzoyl chloride.

Details are given for obtaining large quantities of bromine-free acetylenedicarboxylic acid by Bandrowski's method (this Journ., 1877, ii, 592; compare Michael, A., 1893, i, 144; von Bäcyer, A., 1883, 759, 1198).

Treatment of dibromomaleic acid in pyridine solution with zinc dust yields, in the hot, resinified products, and in the cold only the *pyridine* salt of the acid,  $C_4H_6O_4Br_2C_5NH_5$ , m. p. 120° (decomp.); no indications of the existence of a normal salt were obtained.

Ethyl acetylenedicarboxylate, prepared by esterification of the acid, forms crystals, m. p. 1—2°,  $D_4^2$  (liquid) 1.0690. When prepared by reducing ethyl dibromomaleate with zinc dust, the ester is accompanied by a considerable proportion of resinous matter which cannot be distilled (compare Michael, *loc. cit.*).

The action of hydroxylamine on ethyl acetylenedicarboxylate in presence of sodium ethoxide yields the crystalline, hygroscopic sodium salt,  $NOH \cdot C(ONa) \cdot C(CO_2Na)_2$ , or possibly

$CO_2Na \cdot C(NH \cdot OH) \cdot CH \cdot CO_2Na \rightleftharpoons CO_2Na \cdot C(NOH) \cdot CH_2 \cdot CO_2Na$ , which forms an alkaline, aqueous solution, decolorises permanganate instantaneously, explodes slightly when heated, and with ferric chloride gives the deep violet coloration or precipitate characteristic for hydroxamic acids. Benzoylation by the Schotten-Baumann method gave small proportions of a crystalline compound, which was not examined further. When liberated by the action of dilute acid, the hydroxamic acid itself undergoes decomposition.

Chloroformic chloride,  $COCl \cdot CCl \cdot CH \cdot COCl$  (compare Perkin, T., 1888, 53, 696; Ruggli and Hartmann, this vol., i, 636), prepared by the action of phosphorus pentachloride on acetylene dicarboxylic acid, has b. p. 73—75°/20 mm.

*Dibromofumaric dihydrazide,*



prepared from dibromofumaric chloride and hydrazine hydrate, forms crystals decomposing at about 151°. In this preparation most of the material is converted into a brown powder, which carbonises at a high temperature.

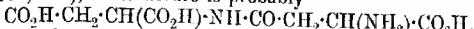
*Dibromofumaric diimide*,  $N_2 \cdot CO \cdot CBr \cdot CBr \cdot CO \cdot N_3$ , obtained by treating the dihydrazide with nitrous acid, forms a white powder, and in the dry state explodes violently when gently rubbed. When heated with alcohol it yields nitrogen and a crystalline compound which is evidently diaminodibromoethylene carbamate, and is to be investigated.

*2:4:5 Tribromo-1-benzoylglutarine*,  $NBz \left< \begin{matrix} CBr \cdot N \\ CBr \cdot CBr \end{matrix} \right>$  forms stout crystals, m. p. 101—102°. T. H. P.

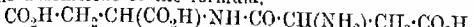
**Dipeptide of Aspartic Acid and Function of Asparagine in Plants.** C. RAVENNA and G. BOSINELLI (*Gazzetta*, 1920, 50, i, 281—288; *Atti R. Accad. Lincei*, 1920, [v], 29, i, 278—289).—When boiled, aqueous solutions of asparagine yield the dipeptide of aspartic acid, together with a little aspartic acid. Neither the latter nor its ammonium salts give the dipeptide under similar conditions (compare this vol., i, 150, 151, 373). The fundamental function of asparagine and of amides of amino acids generally in plants appears to be to render possible the synthesis of polypeptides

and hence that of proteins; the results of the experiments with aspartic acid indicate that direct formation of proteins from the simple amino-acids does not occur.

Since the dipeptide obtained by the authors is formed only from asparagine, to which Piutti ascribes the structure of  $\beta$ -asparagine (A., 1889, 383), its structure is probably

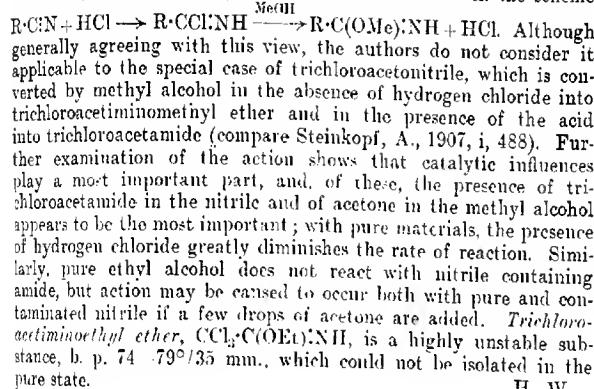


whereas Fischer and Koenigs' dipeptide (A., 1907, i, 486) is probably the  $\alpha$ -isomeride of the formula,



T. H. P.

**Trichloroacetimino-methyl and -ethyl Ethers.** WILHELM STEINKOPF and RUDOLF SEMMIG (*Ber.*, 1920, **53**, [B], 1149—1152).—The conversion of nitriles into imino-ethers has been supposed by Houben (A., 1913, i, 958) to occur in accordance with the scheme



H. W.

**Mercuric Oxycyanide.** A. J. JONES (*Pharm. J.*, 1920, **105**, 87—89).—This compound may be prepared by grinding together 40 grams of mercuric cyanide, 30 grams of yellow mercuric oxide, and 15 c.c. of water for fifteen minutes; 0.5 c.c. of 20% sodium hydroxide is then added, and the stirring continued with the addition of further small quantities of water. After about eighteen hours the mass is diluted with 200 c.c. of water, rendered slightly acid with acetic acid, using phenolphthalein as indicator, and added to 700 c.c. of boiling water containing 20 grams of mercuric cyanide. The mixture is boiled until solution is almost complete, filtered, and cooled. The crystals are collected, washed with a small quantity of cold water, and dried over sulphuric acid. With more concentrated solutions than mentioned above, separated crystals of the oxycyanide are liable to decompose, and explosion has occurred during the preparation of the compound. W. P. S.

**The Preparation of Trimethylarsine and Trimethylarsine Selenide.** R. R. RENSHAW and G. E. HOLM (*J. Amer. Chem. Soc.*, 1920, **42**, 1468—1471).—For the preparation of trimethylarsine two methods were examined. In the first case arsenic trichloride or tribromide was allowed to act on magnesium methyl iodide in ethereal solution, the whole being cooled in ice. By this method apparently at least one other volatile compound, in addition to trimethylarsine, having a stronger and more penetrating odour, was produced. The second method was by the action of arsenic trichloride on zinc methyl in ethereal solution. Owing to the difficulty of separating the ether and the resulting trimethylarsine, it was found advisable to replace the ether by xylene, and then satisfactory yields of pure trimethylarsine, b. p. 51.9—52°/736 mm., D<sup>20</sup> 1.124, were obtained.

When finely powdered selenium was added to the crude ethereal solution of trimethylarsine prepared by the first method, *trimethylarsine selenide*,  $\text{AsMe}_3\text{Se}$ , was obtained. It is very unstable in air, giving off an odour similar to that of trimethylarsine. W. G.

**Process for the Preparation of Arsine Derivatives.** ANDRÉ JOB and HENRI GUINOT (Brit. Pat. 144806).—The nitriles of the general formula  $\text{R}_2\text{AsCN}$ , where R is a fatty or aromatic group, are converted into amides and acids of the type  $\text{AsR}_2\text{CO}\cdot\text{NH}_2$  and  $\text{AsR}_2\text{CO}_2\text{H}$  by the general methods for the hydration of nitriles. For example, cacodyl cyanide is converted into dimethylarsinoformic acid by boiling it with about three times its weight of 50% sulphuric acid for twelve hours. The acid is isolated through its calcium or barium salt and crystallised from acetone and alcohol. Diphenylarsinoformic acid is similarly obtained from diphenylarsine cyanide, or the amide may be first prepared by treating the cyanide in alkaline solution with the theoretical quantity of hydrogen peroxide, and be converted into the acid by subsequent treatment with nitrous acid. Diphenylarsinoformic acid is much less soluble in water than the dimethyl compound. It reddens blue litmus, and forms salts, the majority of which are very soluble in water. G. F. M.

**The Preparation of Zinc Methyl.** R. R. RENSHAW and C. E. GREENLAW (*J. Amer. Chem. Soc.*, 1920, **42**, 1472—1474).—For the preparation of a suitable zinc-copper couple it is recommended to mix nine parts of zinc powder passing a 30-mesh sieve with one part of copper precipitated from solution by zinc, and heat the mixture gradually in a current of hydrogen in a combustion tube, the tube being rotated rapidly, until the zinc turns first a yellow colour and then forms into little pellets of a tarnished lead colour. The heating is then stopped, the couple cooled in hydrogen and used. Methyl acetate is used as a catalyst for the preparation of zinc methyl, 1 c.c. being added to 110 grams of methyl iodide before it is run on to the zinc-copper couple. The mixture is left overnight and then heated at 60° next day, con-

densation being complete in about seven hours. It is noted that at ordinary temperatures zinc methyl iodide dissociates to give enough zinc methyl to cause the vapour above to inflame spontaneously when exposed to the air.

W. G.

**The Energy Content of Polymethylene Rings.** WALTER HÜCKEL (*Ber.*, 1920, **53**, [B], 1277—1283).—The author has applied to polymethylene rings the considerations recently used by Fajans and von Steiger in calculating the heats of combustion of aliphatic and aromatic hydrocarbons (this vol., ii, 354, 355). The heat of combustion of the methylene group in each ring is obtained by dividing the heat of combustion of the necessary compound by the number of carbon atoms contained in it, and the difference between these values and 158 Cal. (the value for the  $\text{CH}_2$  group in a normal carbon chain) is a measure of the abnormal energy content of the rings. In this manner, the values 170, 168.5, 165.5, 159, and 158 are obtained for the methylene group in ethylene, *cyclopropane*, *cyclobutane*, *cyclopentane*, and *cyclohexane* respectively. These results are in good accord with Baeyer's strain theory. Using the formula developed by Fajans (*loc. cit.*), the energy of the C—C linking in the various rings is calculated to 126, 127.2, 130.1, 136.5, 137.5, 138.5, and 139 in ethylene, *cyclopropane*, *cyclobutane*, *cyclopentane*, *cyclohexane*, *cycloheptane*, and *decahydronaphthalene* respectively, the data being in agreement with Baeyer's strain theory as far as the lower members are concerned. The values obtained for methyle*cyclobutane*, methyle*cyclopentane*, and *cycloheptane*, however, require further explanation.

Much of the confusion which has existed with regard to the relative stability of different ring systems is due to inexact comparison. Thus, for example, it has been shown by Berthelot that the union of bromine with *cyclopropane* is accompanied by the development of 9.4 Cal. more than the union of bromine with propylene, and the conclusion is drawn that the *cyclopropane* ring is the more unstable. Actually, the processes are not completely similar, since different types of bond are broken; in the case of propylene, a double bond is opened (energy consumption, 126.5 Cal.), and the other passes into the normal linking (energy evolution, 137.5—126.5 = 11 Cal.), there being thus a total consumption of 115.5 Cal. With *cyclopropane*, the calculated values are: consumption, 127; evolution,  $2(137.5 - 127) = 21$ , or a total consumption of 106 Cal. The difference, therefore, is 9.5 Cal., which agrees excellently with Berthelot's experimental figure. H. W.

**The Phenylpropinenes.** R. LESPIEAU and GARRAU (*Compt. rend.*, 1920, **171**, 111—113).—By the action of benzyl chloride on monosodium acetylidyde, the principal product is the phenylpropinene,  $\text{C}_6\text{H}_5\text{CH}=\text{CMe}$ . If the method of Lepicard and Bourquel (this vol., i, 520) is used, *epidibromohydrin* gives with magnesium phenyl bromide *β-bromo-α-phenylpropylene*,  $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_2$ , m. p. —12.5°, b. p. 102°/17 mm., D<sup>20</sup> 1.39, which when treated

with alcoholic potassium hydroxide at 110° gives the propinene mentioned above. If  $\beta$ -bromo- $\alpha$ -phenylpropylene is brominated, it yields  $\beta\beta\gamma$ -tribromo- $\alpha$ -phenylpropene, b. p. 175°-176°/18 mm., which when reduced with sodium in alcohol gives a compound, which with zinc in alcohol gives an acetylenic hydrocarbon, although the yields throughout are very small. If *epidibromohydrin* is brominated and the resulting tribromopropene,



is condensed with magnesium phenyl bromide in excess, a considerable yield of  $\gamma$ -phenyl- $\Delta$ -propinene,  $\text{CH}_2\text{Ph}\cdot\text{C}\cdot\text{CH}$ , b. p. 70°-71°/20 mm., is obtained, which gives silver and copper derivatives. The cuprous derivative when treated with excess of iodine gives  $\beta\gamma\gamma$ -tri-iodo- $\alpha$ -phenylpropene,  $\text{CH}_2\text{Ph}\cdot\text{CI}\cdot\text{Cl}_2$ , m. p. 84°-85°. W. G.

**Examination of Nitro-compounds by means of Titanium Chloride and Sulphate.** C. F. VAN DUIN (*Rec. trav. chim.*, 1920, **39**, 578-585).—It is recommended to replace the titanium chloride by titanium sulphate in Kuecht's method for determining the nitro-nitrogen in nitro-compounds in the case of feebly substituted compounds.

The author has successfully used titanous chloride for the partial reduction of  $\alpha$ -trinitrobenzene, obtaining a 50% yield of dinitro-aniline.

From a study of the reduction of 2:3:4:6-tetrinitroaniline and of trinitromethylnitroaminophenol by titanous chloride, it is argued that the structure of the nitro-group in position 3 is given by  $\cdot\text{NO}_2$ , and not by  $\cdot\text{O}\cdot\text{NO}$ . W. G.

**The Action of the Grignard Reagent on Aromatic Nitro-compounds.** HARRY HEPWORTH (*T.*, 1920, **117**, 1004-1012).

**Experiments on Halogenation. The Direct Displacement of Negative Groups by Halogen in the Aromatic Series. I. The Displacement of the Nitro-group by Bromine.** SURENDRA NATH DHAR (*T.*, 1920, **117**, 993-1001).

**The Replaceability of Halogens. I. Comparative Replaceability of Chlorine, Bromine, and Iodine in the Halogenonitrobenzenes.** HARTWIG FRANZEN and ERICH BOCKHACKER (*Ber.*, 1920, **53**, [B], 1174-1179).—The data recorded with regard to the relative ease of replacement of the halogens in aromatic compounds are somewhat conflicting, and, as the observations were usually made for preparative purposes, are insufficiently exact to allow any generalisations on the subject. A series of comparative experiments with the halogenonitrobenzenes has therefore been undertaken, the present observations dealing exclusively with alcoholic solutions. In general, the substance (5*M.M.*) is mixed with the base—piperidine, diethylamine, ammonia, sodium ethoxide (25*M.M.*), and either preserved at 0° or at the ordinary tempera-

ture, or heated at the boiling point of the solution or at 100°. The course of the reaction is followed by pouring the solution, after definite intervals of time, into water, adding nitric acid in excess, filtering from precipitated organic matter, and estimating the halogen acid as silver haloid. The results that have been obtained may be summarised as follows. In the cases of the action of diethylamine, piperidine, and sodium ethoxide on the 1-halogeno-2-nitrobenzenes and 1-halogeno-4-nitrobenzenes, iodine is least easily replaced. With diethylamine and piperidine, bromine is more readily replaced than chlorine, but whilst with sodium ethoxide this is also true in the case of *o*-chloronitrobenzene, the reverse holds with *p*-chloronitrobenzene. Reaction of 1-halogeno-2:4-dinitrobenzenes with ammonia, piperidine, aniline, and sodium ethoxide occurs least readily with the iodo-compounds; with ammonia and sodium ethoxide, chlorine is replaced more rapidly than bromine, whilst with piperidine and aniline, bromine reacts more readily than chlorine. There is no general parallelism between the strength of the base and its power of effecting replacement of halogens in the halogenonitrobenzenes in the sense that the stronger base reacts more rapidly than the weaker; the reverse can also be the case.

H. W.

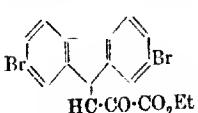
**Some New Derivatives of Mesitylene and  $\psi$ -Cumene.**  
CHARLES STANLEY GIBSON (T., 1920, 117, 948-957).

**Some Nitro-derivatives of Naphthalene and Anthraquinone.** SURENDRA NATH DRAH (T., 1920, 117, 1001-1004).

**The Fluorene Series. II.** ADOLF SIEGLITZ (Ber., 1920, 53, [B], 1232-1241. Compare this vol., i, 27).—The condensation of fluorene with aromatic aldehydes has been further investigated. It is found that 2:7-dibromofluorene reacts with unexpected ease with aromatic aldehydes, yielding products which are solid and characterised by marked ability to crystallise, so that they are very suitable for the identification of the aldehydes. Unfortunately, it does not appear possible to extend the reaction to aliphatic aldehydes or ketones. The colour of the substituted fulvenes is uniformly deeper than that of the substances derived from fluorene itself, but the halochromic colorations with sulphuric acid in the new series are not characteristic. The following individual compounds are described: 9:9'-isophthalidenedifluorene, pale yellow leaflets, m. p. 178-179°; 9-p-bromobenzylidenefluorene, yellow needles, m. p. 144°; 9-m-iodobenzylidenefluorene, yellow, microscopic needles, m. p. 103°; 9-p-iodobenzylidenefluorene, pale yellow, flat prisms, m. p. 121°; 9-piperonylidenefluorene, yellow needles, m. p. 72-73° [picrate, dark red needles with green reflex, m. p. 194-195° (decomp.)]; 9-anisylidenefluorene picrate, red needles, m. p. 121° (decomp.); 9-furylidenefluorene picrate, dark red needles, m. p. 146-147° (decomp.).  
2:7-Dibromofluorene, m. p. 164°, is conveniently prepared by the gradual addition of bromine to an ice-cold solution of fluorene

in chloroform. The condensation products are prepared by adding the calculated amount of the aldehyde dissolved in alcohol (20 c.c.) to a boiling solution of sodium (0.5 gram) and dibromofluorene (1.5 grams) in absolute alcohol (100 c.c.); the solution is rapidly heated to boiling, and subsequently preserved for a day, after which the product is separated; a red substance, probably  $2:2':7:7'$ -tetrabromo- $\alpha\beta$ -dibiphenylene- $1\alpha$ -butadiene, is formed as by-product. The following products are described:  $2:7$ -dibromo-9-benzylidenefluorene, long, pale yellow rods, m. p. 98–99°;  $2:7$ -dibromo-9-*o*-methylbenzylidenefluorene, orange-yellow leaflets, m. p. 141–142°;  $2:7$ -dibromo-9-*m*-methylbenzylidenefluorene, yellow prisms, m. p. 95–96°;  $2:7$ -dibromo-9-*p*-methylbenzylidenefluorene, yellow, matted needles, m. p. 140–141°;  $2:7$ -dibromo-9-*o*-ethylbenzylidenefluorene, yellow prisms and leaflets, m. p. 132–133°;  $2:7$ -dibromo-9-*m*-ethylbenzylidenefluorene, yellow rods, m. p. 82–83°;  $2:7$ -dibromo-9-*p*-isopropylbenzylidenefluorene, yellow needles, m. p. 116–117°;  $2:2':7:7'$ -tetrabromo-9-9'-isophthalylidenedi-9'-fluorene, dark orange leaflets, which do not melt below 300°;  $2:7$ -dibromo-9-*p*-aldehydobenzylidenefluorene, orange-yellow needles, m. p. 218–219°;  $2:2':7:7'$ -tetrabromo-terephthalylidenedi-9'-fluorene, dark orange leaflets, which do not melt below 300°;  $2:7$ -dibromo-9-*o*-chlorobenzylidenefluorene, not melt below 300°;  $2:7$ -dibromo-9-*m*-chlorobenzylidenefluorene, pale yellow, microcrystalline needles, m. p. 136–137°;  $2:7$ -dibromo-9-*p*-chlorobenzylidenefluorene, long, yellow, matted needles, m. p. 211–212°;  $2:7$ -dibromo-9-*m*-bromo-benzylidenefluorene, small, yellow needles, m. p. 152–153°;  $2:7$ -dibromo-9-*p*-iodobenzylidenefluorene, orange-yellow needles, m. p. 207–208°;  $2:7$ -dibromo-9-*o*-methoxybenzylidenefluorene, orange-yellow leaflets, m. p. 154–155°;  $2:7$ -dibromo-9-*p*-methoxybenzylidenefluorene, deep yellow needles, m. p. 132–133°;  $2:7$ -dibromo-9-piperonylidenefluorene, yellow needles, m. p. 159–160°;  $2:7$ -dibromo-9-*o*-nitrobenzylidenefluorene, orange-yellow needles, m. p. 201–202°;  $2:7$ -dibromo-9-*m*-nitrobenzylidenefluorene, small, yellow crystals, m. p. 154–155°;  $2:7$ -dibromo-9-*p*-nitrobenzylidenefluorene, orange-yellow, microcrystalline powder, m. p. 195–196°;  $2:7$ -dibromo-9-*2'*-chloro-5'-nitrobenzylidenefluorene, yellow needles, m. p. 212–213° after softening at 190° (m. p. 216–218° after resolidification);  $2:7$ -dibromo-9-cinnamylidenefluorene, slender, deep yellow needles, m. p. 206–207°;  $2:7$ -dibromo-9-furylidenefluorene, long, greenish-yellow needles, m. p. 190–191°.

Ethyl oxalate condenses with  $2:7$ -dibromofluorene in the presence of sodium ethoxide to form ethyl  $2:7$ -dibromofluorenecarboxylate (annexed formula), shining, yellow needles, m. p. 176°; the substance gives a brown coloration with ferric chloride, and yields a benzyl derivative, canary-yellow rods, m. p. 152–153°.



**cycloHexylamines.** II. A. SKITA and H. ROLFS (*Ber.*, 1920, 53, [B], 1242—1255. Compare Skita and Berendt, this vol., i, 27).—In connexion with Skita's process for the reduction of aromatic amines to *cyclohexylamines*, the general behaviour of the latter class of substances has been more fully investigated.

[With KARL HILS and GUSTAV KIRCHHOFF].—Ammonium *dicyclohexyl dithiocarbamate*,  $C_6H_{11}\cdot NH\cdot CS\cdot S\cdot NH_3\cdot C_6H_{11}$ , m. p. 160°, is readily prepared by the direct union of *cyclohexylamine* and carbon disulphide; it is converted by distillation with an aqueous solution of mercuric chloride into *cyclohexylthiocarbamide*, b. p. 219°/746 mm., which may also be obtained by the distillation of *dicyclohexylthiocarbamide*, cubes, m. p. 180—181°, with glacial phosphoric acid. *cycloHexylthiocarbamide* combines with ammonia to yield *cyclohexylthiocarbamide*,  $NH_2\cdot CS\cdot NH\cdot C_6H_{11}$ , m. p. 161—162°, with aniline to give *phenylcyclohexylthiocarbamide*, m. p. 150—151°, and with absolute alcohol at 100° to form *cyclohexylthiourethane*, m. p. 45—46°.

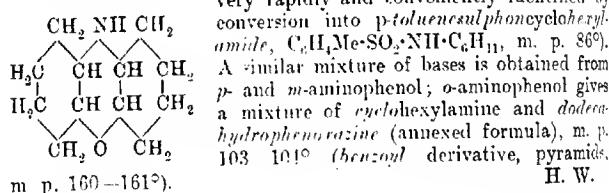
*Dicyclohexylcarbamide*, m. p. 229—230°, is obtained from *cyclohexylamine* and carbonyl chloride, and is converted by phosphoric oxide into *cyclohexylcarbamide*,  $C_6H_{11}\cdot N\cdot CO$ , b. p. 175°/750 mm.; the latter is transformed by ammonia, aniline, and ethyl alcohol into *cyclohexylcarbamide*, m. p. 184°, *phenylcyclohexylcarbamide*, colourless needles, m. p. 182°, and *cyclohexylurethane*, m. p. 57°.

*cycloHexylamine* is converted by methyl sulphate in warm ethereal solution into *cyclohexylamine methyl sulphate*, m. p. 103°, and a basic portion, which, after purification through the *acetyl* derivative, b. p. 249°/740 mm., or the *benzoyl* derivative, needles, m. p. 76°, yields *N-methylcyclohexylamine*, b. p. 147°, identical in all respects with the product obtained previously (*loc. cit.*) by the catalytic hydrogenation of methylaniline. It was further identified by conversion into the *picrate*, m. p. 170°, and into *nitroso-N-methylcyclohexylamine*, yellow liquid, b. p. 121°/12 mm. (*hydrochloride*, needles, m. p. 176°). *N*-Dimethylcyclohexylamine, b. p. 165°, is prepared in 80% yield by the action of formic acid and formaldehyde on *cyclohexylamine* at 120°; the *picrate* has m. p. 181°. The base is converted by methyl iodide into *trimethylcyclohexylammonium iodide*, needles, m. p. 277°, which is transformed by silver oxide into the corresponding *hydroxide*, which decomposes into tetrahydrobenzene, trimethylamine, and water when its aqueous solution is evaporated. When treated with nitrosyl chloride in cold ethereal solution, *N*-dimethylcyclohexylamine undergoes a remarkable change, whereby *N-nitroso-N-methylcyclohexylamine* is produced; the latter is reduced by tin and hydrochloric acid to *N-methylcyclohexylamine*. A similar instance is presented by *N*-methyl*dicyclohexylamine*,  $C_6H_{11}\cdot NM_2\cdot C_6H_{11}$ , which with nitrosyl chloride gives *nitrosodicyclohexylamine*,  $C_6H_{11}\cdot N(NO)\cdot C_6H_{11}$ , m. p. 105°, which is reduced to *dicyclohexylamine* by zinc and hydrochloric acid.

Ethyl iodide reacts readily with *cyclohexylamine*, giving *N*-ethyl-*cyclohexylamine*, identical with the product obtained by the cata-

lytic reduction of ethylaniline (*loc. cit.*); the *benzoyl* and *acetyl* derivatives have b. p.'s  $201^\circ$  and  $256^\circ/740$  mm. respectively, whilst the *picrate*, yellow crystals, and *hydrochloride*, have m. p.'s  $133^\circ$  and  $184^\circ$  respectively. *Nitroso-N-ethylcyclohexylamine* is an oil, b. p.  $130^\circ/12$  mm. When treated with ethyl iodide and potassium hydroxide, *cyclohexylamine* is transformed into *N-diethylcyclohexylamine*, b. p.  $193^\circ$ .

*Acetanilide* is but little attacked by hydrogen under conditions similar to those adopted for the reduction of aniline to *cyclohexylamine*; by increasing the concentration of the catalyst and raising the temperature to  $70$ — $80^\circ$ , it can be completely hydrogenated to *acetyl-cyclohexylamine*, m. p.  $107^\circ$ . Under similar conditions, the isomeric *acetotoluidides* can be completely converted into their hexahydro-derivatives; *acetyl-2-methylcyclohexylamine* has b. p.  $154^\circ/20$  mm., m. p.  $50^\circ$ , the corresponding *3-derivative* has b. p.  $152^\circ/18$  mm., m. p.  $74$ — $75^\circ$ , whilst the *4-compound* has b. p.  $152^\circ/12$  mm., m. p.  $77$ — $78^\circ$ . *p-Ethoxyacetanilide* is hydrogenated with remarkable ease, but the product is *acetyl-cyclohexylamine*, m. p.  $106$ — $107^\circ$ . The elimination of the ethoxy group is the more noteworthy since anisole and phenetole are reduced to *cyclohexyl methyl ether*, b. p.  $140^\circ/740$  mm., and *cyclohexyl ethyl ether*, b. p.  $114$ — $145^\circ/738$  mm., under precisely similar conditions. Anisidine and phenetidine are, however, converted into a mixture of *cyclohexylamine* and *cyclohexylamine* (small quantities of the latter are

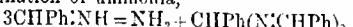


**Crystalline Form of 2:4-Dichloro-3-nitroacetanilide.**  
MARIA DE ANGELIS (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 247—251).—This compound is dinorphous; both the  $\alpha$ - and  $\beta$ -modifications form crystals belonging to the prismatic class of the monoclinic system; for the former,  $a:b:c = 1:1507:1$ ;  $\alpha = 1348^\circ$ ,  $\beta = 66^\circ 23'$ , and for the latter,  $a:b:c = 1:5792:1$ ;  $\beta = 62^\circ 23'$ . T. H. P.

**Catalysts which Promote Reaction between Aniline and Ethyl Alcohol.** T. B. JOHNSON, A. J. HILL, and J. J. DONLEAVY (*J. Ind. Eng. Chem.*, 1920, **12**, 636—644).—No alkylation results when aniline is heated with ethyl alcohol in an autoclave in the presence of calcium oxide. Aniline hydrochloride heated with ethyl alcohol for eight hours in an autoclave at  $175$ — $180^\circ$ , in the presence of sodium bromide, cupric chloride, and calcium chloride, gives good yields of diethylaniline containing only about 5% of mono-

ethylaniline. Substitution of aniline for an equivalent quantity of aniline hydrochloride yields a product largely composed of monoethylaniline. Zinc chloride probably has a dealkylising action as well as a dehydrating effect, and is less effective as a catalyst than calcium chloride, whilst potassium iodide is slightly more effective than sodium bromide. The use of 95% alcohol instead of absolute ethyl alcohol causes the yield of diethylaniline to be lowered by about 7%. The addition of the sodium bromide has the effect of lowering the amount of monoethylaniline by about 2%, whilst pyridine has a negative catalytic action, and raises it by about 11% (compare *J. Soc. Chem. Ind.*, 1920, September). C. A. M.

**Catalytic Hydrogenation of Nitriles; Mechanism of the Formation of Secondary and Tertiary Amines.** GEORGES MIGNONAC (*Compt. rend.*, 1920, **171**, 114-117).—When benzonitrile is hydrogenated in absolute alcohol in the presence of nickel as catalyst at the ordinary temperature (compare this vol., i, 442), the operation being interrupted when one molecule of hydrogen has been fixed, the product consists of one part of benzylamine and 2-25 parts of benzylidenebenzylamine,  $\text{CHPh:N}\cdot\text{CH}_2\text{Ph}$ , the latter, if the hydrogenation is continued, being converted into dibenzylamine. The course of the reaction is considered to be that benzaldimine is first formed, and that this then rapidly condenses with the elimination of ammonia,



and that the condensation product then undergoes hydrogenation, giving benzylamine and benzylidenebenzylamine.

Under similar conditions, *o*-toluonitrile gives *o*-methylbenzylamine and *o*-methylbenzylidene-*o*-methylbenzylamine, b. p. 170-171°/5 mm., and *p*-toluonitrile gives *p*-methylbenzylamine and *p*-methylbenzylidene-*p*-methylbenzylamine, m. p. 83-84°, b. p. 160°/3.5 mm.

W. G.

**Hydrogenation in the Naphthalene Series.** F. M. ROWE (*J. Soc. Chem. Ind.*, 1920, **39**, 241-246).— $\alpha$ -Naphthylamine is reduced by sodium and amyl alcohol to *ar*-tetrahydro- $\alpha$ -naphthylamine, but, in the presence of ethyl or butyl alcohol, only dihydro-derivatives are formed. Preliminary experiments indicate that this difference cannot be ascribed solely to differences in temperature of the experiment. A similar result is observed when reduction is effected in the presence of an indifferent solvent, such as toluene or solvent naphtha (compare D.R.-P. 305347, 306724). A more extended study shows that  $\alpha$ -naphthylamine is reduced by sodium and an alcohol to 5:8-dihydro-1-naphthylamine; the latter, under suitable conditions of temperature and alkali alkylxoxide concentration, undergoes isomerisation to 7:8-dihydro-1-naphthylamine, which, unlike the 5:8-isomeride, is further reduced to *ar*-tetrahydro- $\alpha$ -naphthylamine. The failure to obtain the tetrahydro-compound when amyl alcohol was not used is probably to be explained by the absence of conditions suitable for the isomerisa-

tion. Reduction of naphthalene takes place similarly to that of  $\alpha$ -naphthylamine; 1:4-dihydronaphthalene is initially formed, which, under suitable conditions, is isomerised to 1:2-dihydronaphthalene and then reduced to tetrahydronaphthalene.

The direct hydrogenation of naphthalene and  $\alpha$ -naphthylamine has also been studied, the experiments being performed by bubbling hydrogen at the ordinary pressure through the purified substance, either molten or dissolved in a suitable solvent, in presence of nickel deposited on kieselguhr, in a glass vessel fitted with a condenser and an agitator capable of being driven at a high speed. Temperatures varying from 100° to the respective boiling points of naphthalene and  $\alpha$ -naphthylamine were used with these substances in the absence of a solvent without result, except that there was an appreciable evolution of ammonia in the latter case, particularly at the higher temperatures. Negative results were also obtained with  $\alpha$ -naphthylamine dissolved in boiling light petroleum, toluene, or solvent naphtha. The base, however, was reduced in boiling ethyl-alcoholic solution or, preferably, in boiling mixtures of ethyl alcohol with toluene or solvent naphtha; in the latter circumstances, 5:8-dihydro- $\alpha$ -naphthylamine was quantitatively formed, but the further reduction to tetrahydro- $\alpha$ -naphthylamine was not satisfactorily accomplished. Similarly, naphthalene could be hydrogenated in boiling ethyl-alcoholic solution, a mixture of products being invariably obtained, the main constituent of which is 1:4-dihydronaphthalene; prolongation of the action or treatment of 1:4-dihydronaphthalene in boiling ethyl-alcoholic solution led to the formation of some tetrahydronaphthalene, together with a mixture of liquids of lower boiling point which was not examined more closely, but probably consisted of more completely saturated derivatives.

H. W.

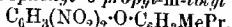
**Spontaneous Decomposition of  $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane. II.** S. BERLINGOZZI (*Gazzetta*, 1920, 50, i, 321-325. Compare this vol., i, 180).— $\alpha$ -Aminophenyl- $\alpha$ -naphthylmethane undergoes spontaneous decomposition at the ordinary temperature, with liberation of ammonia and formation of *di-(naphthylbenzyl) amine*,  $\text{NH}(\text{CHPh-C}_9\text{H}_7)_2$ , which forms minute, shining, white crystals, m. p. 181°. It is shown that the product, m. p. 121°, described by Busche and Leefhelm (A., 1908, i, 152) as  $\alpha$ -aminophenyl- $\alpha$ -naphthylmethane, consists of a mixture of the latter with *di-(naphthylbenzyl) amine*.

T. H. P.

**Oxynitration of Benzene [Formation of Nitrophenols].** LÉO VIGNON (*Bull. Soc. chim.*, 1920, [iv], 27, 547-550).—To obtain the best yield of nitrophenols in the action of nitric acid and mercuric nitrate on benzene it is advisable to use an excess of benzene, and the following proportions are recommended: 1000 grams of nitric acid (D 1.29-1.325), 25 grams of mercuric nitrate, and 500 grams of benzene, the mixture being heated on a water-bath for five to seven hours.

W. G.

**Derivatives of Diphenyl Ether.** ALFRED N. COOK, WM. C. EVANS, and DANIEL SHERK (*Proc. S. Dak. Acad. Sci.*, 1917, **2**, 21–25).—*2:4-Dinitrophenyl 6-propyl-m-tolyl ether*,



sulphur-yellow needles, m. p. 64°, obtained by heating equal molecular quantities of potassium thymolate and 1-bromo-2:4-dinitrobenzene, yields on sulphonation a *monosulphonic acid*, pearly crystals (*lead salt*; *barium salt* with 5.5H<sub>2</sub>O). *2-Nitrophenyl 5-propyl-o-tolyl ether*, brownish-red liquid, b. p. 222°/20 mm., forms a *sulphonic acid*, crystals with 2H<sub>2</sub>O, m. p. 223–227° (decomp.), of which the *barium*, *calcium*, and *lead* salts crystallise with 3, 6, and 8H<sub>2</sub>O respectively.

## CHEMICAL ABSTRACTS.

**Derivatives of the Sulphone of o-Cresol (o-Hydroxytolylsulphone).** FRÉDÉRIC REVERDIN and ANDRÉ ROETHLISBERGER (*Helv. Chim. Acta*, 1920, **3**, 486–492).—The authors have prepared *o-hydroxytolylsulphone* by Zehenter's method (A., 1912, i, 444), and have studied certain of its derivatives.

The acetyl compound agrees in properties with Tassinari's product (A., 1889, 245). The *benzoyl* derivative, SO<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>Me·OBz)<sub>2</sub>, prepared by either Schotten and Baumann's or Reverdin's method (A., 1918, i, 536), forms colourless, prismatic crystals, m. p. 183–184°. The dinitro-derivative, m. p. 243° (compare Zehenter, *loc. cit.*), yields an *acetyl* compound, SO<sub>2</sub>(NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Me·OAc)<sub>2</sub>, which forms deep yellow crystals, m. p. 204–205°, and a *benzoyl* compound, SO<sub>2</sub>(NO<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>Me·OBz)<sub>2</sub>, m. p. 179–180°.

When treated with sulphuric acid (20% SO<sub>3</sub>), the dinitro-derivative is converted into an *isomeride*, C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>S, which forms yellow crystals, m. p. 209–210°, and yields an *acetyl* derivative, crystallising in pale yellow plates, m. p. 200–201°.

Nitration of the acetyl derivative of the sulphone yields partly the acetyl dinitro-compound, melting at 243°, but is incomplete, and, if carried further, is accompanied by partial scission of the molecule. Nitration of the benzoyl derivative yields mainly a *m-nitrobenzoyl-o-cresolsulphone*, the nitro-group being introduced into the benzoyl residue.

Reduction of the dinitro-derivative, m. p. 243°, by means of tin and hydrochloric acid gives a double chloride of tin and the *aminosulphone*; the free *aminosulphone* forms pale brown needles, m. p. 212° (decomp.), is readily oxidised, gives solutions which colour in the air and yield a deep brown coloration with ferric chloride solution, and furnishes a highly stable *diaz*-derivative, crystallising in yellow needles. The compound obtained on reduction of the isomeric dinitro-compound, m. p. 209–210°, is not oxidised in solution by atmospheric oxygen, and yields a less stable *diaz*-derivative.

T. H. P.

**Derivatives of Trihalogen Tertiary Butyl Alcohol. III. The Benzoic Acid Ester of Trichloro-*tert*-butyl Alcohol or Chlorotetone Benzoic Ester.** T. B. ALDRICH (*J. Amer. Chem. Soc.*, 1920, **42**, 1502–1507. Compare A., 1916, i, 115; 1917, i, 77; 1919, i, 62).—A repetition of the work of Willgerodt and Dürr

(compare *J. pr. Chem.*, 1889, [ii], **39**, 286). It is now found that when molecular proportions of benzoyl chloride and chloroetone (trichloro-*tert*-butyl alcohol) are heated together on a water-bath until hydrogen chloride ceases to be given off, trichloro-*tert*-butyl benzoate is obtained, and may be isolated in a crystalline form, m. p. 34—35°. It may be distilled under reduced pressure without appreciable decomposition, and is not readily hydrolysed, being much more stable than other esters of this alcohol. Pharmacological tests indicate that it possesses less hypnotic or anaesthetic properties, and is less toxic than the esters studied thus far (*loc. cit.*). W. G.

**Amino-alcohols. Action of Amines on the Mono-esters (Acetates and Benzoates) of Chlorohydrins.** E. FOURNEAU and (MME) P. RAMART-LUCAS (*Bull. Soc. chim.*, 1920, [iv], **27**, 550—557).—Sodium benzoate acts on  $\alpha$ -chloropentan- $\gamma$ -ol in the presence of potassium iodide to give  $\alpha$ -benzoylory/pentan- $\gamma$ -ol, b. p. 171°/11 mm., 181°/20 mm., which with thionyl chloride in pyridine solution yields  $\gamma$ -benzoylory/pentan- $\alpha$ -ol, b. p. 165—167°, 17 mm., 157—159°/12 mm. This chloro-ester when warmed with dimethylamine in benzene solution gives  $\alpha$ -dimethylamino- $\gamma$ -benzoyloxy/pentane, b. p. 170° 16 mm., which may also be obtained by the action of benzoyl chloride on  $\alpha$ -dimethylaminopentan- $\gamma$ -ol. When  $\alpha$ -chloropentan- $\gamma$ -ol is heated for four hours at 160—170° with potassium acetate it yields  $\gamma$ -acetoxypentan- $\alpha$ -ol, b. p. 113—114°/12 mm., which, with thionyl chloride, gives  $\alpha$ -chloro- $\gamma$ -acetoxypentane, b. p. 81—86°/14 mm. This chloroacetate with dimethylamine gives a mixture of bases, from which  $\alpha$ -dimethylamino- $\gamma$ -acetoxypentane can be isolated.  $\gamma$ -Chloro- $\alpha$ -phenylpropan- $\beta$ -ol with sodium benzoate gives a mixture of two benzoates, from which the chloro-compound can be prepared, and this with dimethylamine gives two bases, namely,  $\gamma$ -dimethylamino- $\alpha$ -phenylpropan- $\beta$ -ol, b. p. 153°/40 mm., and its benzoate, b. p. 220°/20 mm.

$\gamma$ -Chloro- $\alpha$ -phenylpropan  $\alpha$ -ol gives with sodium benzoate a benzoate, b. p. 230°/12 mm., which when treated with thionyl chloride, and then with dimethylamine, yields  $\gamma$ -dimethylamino- $\gamma$ -phenylpropyl benzoate, b. p. 230°/15 mm., giving a hydrochloride, m. p. 146°. W. G.

**The Preparation of *o*-Nitrobenzoic Acid.** MARIE REIMER and ELIZABETH STEWART GATEWOOD (*J. Amer. Chem. Soc.*, 1920, **42**, 1475—1478).—The mixed *o*- and *p*-nitrotoluenes obtained from the nitration of toluene were oxidised by alkaline permanganate in concentrated solution (compare Bigelow, this vol., i, 20). The *o*- and *p*-nitrobenzoic acids were isolated by conversion into their methyl esters, which were then separated by fractional distillation under reduced pressure. W. G.

***o*-Sulphobenzoic Anhydride and Benzamide- and Methylbenzamide-*o*-sulphonic Acids.** H. J. TAVERNE (*Rec. trav. chim.*, 1920, **39**, 542—548).—*o*-Sulphobenzoic anhydride was prepared by

the interaction of potassium hydrogen sulphonate and phosphorus pentachloride, and by the action of acetyl chloride on the free acid. The anhydride prepared by either method had m. p. 130°, and molecular-weight determinations showed it to be an internal anhydride. By the action of dry ammonia on its benzene solution, it gave ammonium benzamide-*o*-sulphonate, from which the corresponding barium salt,  $(\text{NH}_2\text{CO-C}_6\text{H}_4\text{SO}_3)_2\text{Ba}\cdot 6\text{H}_2\text{O}$ , was obtained, and this, on decomposition with dilute sulphuric acid, gave the free acid, m. p. 186°, giving a silver salt,  
 $\text{NH}_2\text{CO-C}_6\text{H}_4\text{SO}_3\text{Ag.H}_2\text{O}$ .

When a benzene solution of *o*-sulphobenzoic anhydride is saturated with methylamine, a crystalline precipitate of *methylammonium methylbenzamide-*o*-sulphonate*,  
 $\text{NHMeCO-C}_6\text{H}_4\text{SO}_3\text{NMe}_2$ ,

m. p. 189—190°, is obtained. This gives the corresponding barium salt,  $(\text{C}_5\text{H}_5\text{O}_4\text{NS})\text{Ba}\cdot 4\text{H}_2\text{O}$ , which, on decomposition with sulphuric acid, gives *methylbenzamide-*o*-sulphonic acid*, m. p. 167—169°.

W. G.

**Catalytic Hydration of Nitriles.** A. MAILHE (*Compt. rend.*, 1920, **171**, 245—247).—Nitriles may be converted into the corresponding acids by passing their vapours, along with water vapour, over thorium oxide at a temperature of 420°. W. G.

**Boiling Points of Esters of Stereoisomeric Cinnamic Acids.** R. STOERMER and KARL SANDOW (*Ber.*, 1920, **53**, [B], 1283—1289).—It was observed by Stoermer, Grimm, and Laage (A., 1917, i, 647) that the esters of *cis*-cinnamic acids uniformly boil about 12—15° lower than the esters of the corresponding stereoisomeric *trans*-acids, and that, as far as the evidence was available, this relationship held good even in those cases in which the *cis*-acid had a higher melting point than the *trans*-acid. The number of such instances was, however, somewhat restricted; in order, therefore, to secure further evidence on this point, the authors have prepared a further series of such pairs of acids, and have found their previous observation completely confirmed. The boiling points of the esters of stereoisomeric cinnamic acids appear to be a valuable criterion of the adherence of the free acid to the *allo*-series or otherwise. The alkoxy- $\beta$ -methylcinnamic acids are obtained from 4-methylcoumarin by fission and subsequent alkylation, or by transformation of the *cis*-forms primarily obtained into the corresponding *trans*-forms by concentrated potassium hydroxide solution. Esterification of the acids is conveniently effected with methyl or ethyl sulphate in alkaline solution. The following substances are described: *trans*-*o*-hydroxy- $\beta$ -methylcinnamic acid, m. p. 160° (methyl ester, m. p. 143°); *trans*-*o*-methoxy- $\beta$ -cinnamic acid

$\text{OMe-C}_6\text{H}_4\text{CMe}$  (I), m. p. 96° (compare

$\text{H-CO}_2\text{H}$   $\text{Me-C}_6\text{H}_4\text{OMe}$  Stoermer, Grimm, and

(I).  $\text{H-CO}_2\text{H}$  Laage, *loc. cit.*), *methyl*

(II).  $\text{H-CO}_2\text{H}$  *ester*, b. p. 178—179°/

$\beta$ -methyleinnamic acid (II), m. p. 123°, *methyl ester*, b. p. 164°/

28 mm., m. p. 44°; *trans*-*o*-*ethoxy*- $\beta$ -*methylcinnamic acid*, m. p. 111—112°, *methyl ester*, b. p. 160—161°/13 mm., m. p. 43°, *ethyl ester*, m. p. 53°, *amide*, m. p. 97°; *cis*-*o*-*ethoxy*- $\beta$ -*methylcinnamic acid*, m. p. 138°, *methyl ester*, b. p. 148—148.5°/13 mm., *ethyl ester*, b. p. 152°/11 mm., *amide*, m. p. 118°; *trans*-*o*-*n-propoxy*- $\beta$ -*methylcinnamic acid*, slender needles, m. p. 72°, *methyl ester*, b. p. 177°/20 mm.; *cis*-*o*-*n-propoxy*- $\beta$ -*methylcinnamic acid*, m. p. 108°, *methyl ester*, b. p. 167°/20 mm.; *trans*-*o*-*n-butoxy*- $\beta$ -*methylcinnamic acid*, colourless needles, m. p. 57°, *methyl ester*, b. p. 187—188°/24 mm.; *cis*-*o*-*n-butoxy*- $\beta$ -*methylcinnamic acid*, m. p. 74°, *methyl ester*, b. p. 175°/24 mm. H. W.

**Boiling Points of Esters of Stereoisomeric Unsaturated Acids.** R. STOERNER and H. KIRCHNER (*Ber.*, 1920, 53, [B], 1289—1299).—In previous communications (Stoermer, Grimm, and Laage, *A.*, 1917, i, 647. Stoermer and Sandow, preceding abstract) it has been shown that the esters of the *cis*-form of stereoisomeric unsaturated cinnamic acids have a lower boiling point than the corresponding *trans*-compounds. The observations are now extended to the halogenated cinnamic acids, and the same regularity is observed in all cases in which the configuration of the acids can be regarded as definitely elucidated. In all, therefore, nineteen pairs of stereoisomeric esters have been investigated without leading to the discovery of an exception to the rule. Up to the present, however, only aromatic compounds have been considered; an attempt is therefore made to extend the observations to aliphatic compounds, and fumaric and maleic esters are chosen by reason of the close analogy in chemical behaviour of the phenyl and carboxyl groups. In this case, however, an exception appears to be presented which leads the authors to consider that methyl maleate may possibly have the annexed constitution; a certain amount of evidence in favour of this view is derived from spectrochemical observations and from analogy to the corresponding chlorides. The melting point of the free acids appears to be a very uncertain criterion of their adherence to the *cis*- or *trans*-series; still less reliance can be placed on the melting points of their esters or amides in this respect. It is interesting to note that the position of the halogen atom in the  $\alpha$ - and  $\beta$ -halogenated acids is practically without influence on the boiling points of the esters. The following compounds are described. *trans*- $\alpha$ -chlorocinnamic acid, m. p. 33—34°, *methyl ester*, b. p. 167° (corr.)/28 mm., 108—109°/0.5 mm.; *methyl cis*- $\alpha$ -chlorocinnamate, b. p. 153—154°/28 mm., 98—99°/0.6 mm.; *methyl trans*- $\alpha$ -bromocinnamate, m. p. 23°, b. p. 177—178° (corr.)/23 mm., 120—121°/0.6 mm.; *methyl cis*- $\alpha$ -bromocinnamate, b. p. 167.5—168.5° (corr.)/26 mm., 111°/0.6 mm.; *trans*- $\alpha$ -chlorocinnamamide, m. p. 121°, b. p. 216—217°/12 mm. (with partial sublimation), 158—160°/0.6 mm.; *cis*- $\alpha$ -chlorocinnamamide, m. p. 134°, b. p. 210°/13 mm., 153—154°/0.6 mm.; *trans*- $\alpha$ -bromocinnamamide,

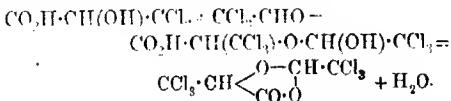
m. p. 117—118°, b. p. 212—213°/13 mm. (partial decomp.); *cis*- $\alpha$ -bromocinnamamide, m. p. 129°, b. p. 215—216°/13 mm. The  $\alpha$ -iodocinnamic acids (compare Bougault, A., 1916, i, 817) are obtained by the action of a solution of iodine in potassium iodide on the semicarbazone of phenylpyruvic acid in the presence of alkali, and are separated by taking advantage of the differences in their strengths; the *trans*-acid forms colourless leaflets, m. p. 162—163°, and yields a *methyl* ester, b. p. 132—133° (corr.)/0·4 mm., whilst the *cis*-acid forms yellow crystals, m. p. 110—111°, and gives a *methyl* ester, b. p. 114—115° (corr.)/0·4 mm. *Methyl trans*- $\beta$ -chlorocinnamate, m. p. 29°; *methyl cis*- $\beta$ -chlorocinnamate, m. p. 34°, b. p. 96—97° (corr.)/0·5 mm.; *methyl trans*- $\beta$ -bromocinnamate, b. p. 122°/0·6 mm.; *methyl cis*- $\beta$ -bromocinnamate, colourless needles, m. p. 56°, b. p. 110—111°/0·6 mm.; *methyl trans*- $\alpha\beta$ -dichlorocinnamate, b. p. 121°/0·6 mm.; *methyl cis*- $\alpha\beta$ -dichlorocinnamate, b. p. 113°/0·6 mm., *methyl trans*- $\alpha\beta$ -dibromocinnamate, hexagonal rods, m. p. 64—65°, b. p. 138°/0·5 mm.; *methyl cis*- $\alpha\beta$ -dibromocinnamate, b. p. 124°/0·5 mm.

Attempts to obtain *cis*- $\beta$ -ethoxycinnamic acid are described. On one occasion a small amount of an acid, m. p. 78°, was isolated from the products of hydrolysis of ethyl  $\beta$ -ethoxycinnamate, which is possibly the desired substance, but the preparation could not be repeated. *trans*- $\beta$ -Ethoxycinnamic acid is extensively decomposed when its solution in benzene is exposed to ultra-violet light, ethoxystyrene being produced. Under similar treatment, the ethyl ester is considerably resinified, but on distillation of the product, a fraction of lower boiling point was obtained which yielded an acid, m. p. 70—80°, in small amount. Sodium  $\beta$ -ethoxycinnamate became completely resinified when illuminated. Similar observations with  $\beta$ -phenoxyacrylic acid and its ester are recorded. H. W.

**Optically Active Cinnamic Acids and the Cinnamates of Tartaric Acid which are Produced at the Formation of the Former.** EMIL ERLENMEYER and GUSTAV HILGENDORFF (*Biochem. Zeitsch.*, 1920, **103**, 79—123).—Tartaric acid was fused with cinnamoyl chloride, cinnamic anhydride, and cinnamic acid respectively at 168—170°. The cinnamic acid was extracted from the fused mass with light petroleum. The acid thus obtained was optically active. The highest activity was manifested by the cinnamic acid obtained by extracting the product of fusion of cinnamic anhydride with tartaric acid. The residues obtained by extracting the fused masses with light petroleum were further extracted with ether, yielding a colloidal fraction which was again fractionated either by extraction with benzene or by treating it with sodium carbonate, gradually acidifying, and extracting the successive fractions with ether. The various fractions thus obtained containing mixtures of cinnamates showed a carbon content varying from 55·76%, which represents the carbon content of the monocinnamates, to 64·39%, which is that of the dicinnamates. The lowest rotation was shown by the cinnamates obtained from the fusion

with cinnamic acid, the highest rotation by those obtained with cinnamoyl chloride. An intermediate value was shown by cinnamates from the anhydrides. This is explained by the presence of large quantities of the highly active dicinnamate in the chloride mixture and the absence of the less active monocinnamate, which is, however, present in the anhydride fusion and more so in the cinnamic acid fusion. A colloidal monodicinnamate ( $\alpha_D -120^\circ$  approximately) was also obtained from the cinnamoyl chloride fusion. Cinnamates with a similar number of carbon atoms, but of a higher rotation, were obtained from the anhydride and from the cinnamic acid fusions. These masses also yielded a fraction of the same carbon content as the dicinnamates, but of a considerably lower rotation. It is suggested that the optical activity of the cinnamic acid extracted from the cinnamic anhydride fusion is due to the "induction" influence of the cinnamates formed. S. S. Z.

**Benzyllic Acid and Aldehydes.** A. BISTRZYCKI and BRUNO BRENKEN (*Helv. Chim. Acta*, 1920, **3**, 468—472).—The authors have shown (see this vol., i. 630) that, whereas 1 mol. of thioglycollic acid condenses with 2 mols. of an aldehyde, 1 mol. of thienzylic acid condenses with only 1 mol. of an aldehyde. The experiments now described show that benzyllic acid acts on aldehydes in the same way as aliphatic hydroxy-acids or thiobenzyllic acid. According to Wallach (A., 1878, 288), the first stage in the formation of chloralide by the interaction of trichlorolactic acid and anhydrous chloral consists in the conversion of the acid into trichlorolactide, which then reacts with the chloral. The authors, however, consider it more probable that the reacting compounds first form an additive compound comparable with chloral acetate, decomposition with loss of water then taking place:



The *methylene ether ester of benzyllic acid*,  $\text{CPh}_2 \begin{array}{l} \text{O}-\text{CH}_2 \\ \swarrow \quad \searrow \\ \text{CO}\cdot\text{O} \end{array}$ , prepared by the interaction of benzyllic acid and formaldehyde, forms transparent, rhomboidal plates often with truncated angles, softening a little below its m. p.,  $43-44^\circ$ . The powdered substance is converted into deep blue flocks by concentrated sulphuric acid, the latter turning first green and then colourless. It is appreciably more stable than the corresponding ester of glycollic acid (compare de Bruyn and van Ekenstein, A., 1902, i, 76; 1903, i, 149), from which it is derived.

The *benzylidene ether ester*,  $\text{CPh}_2 \begin{array}{l} \text{O}-\text{C}\text{HPh} \\ \swarrow \quad \searrow \\ \text{CO}\cdot\text{O} \end{array}$ , obtained from benzyllic acid and benzaldehyde, crystallizes in bundles of flat, microscopic prisms, m. p.  $91-95^\circ$ , and dissolves in concentrated sulphuric

acid, giving a violet-red solution, which shows a faint greenish-brown fluorescence. This compound also exhibits marked stability.

Attempts to couple acetone with benzylic acid were unsuccessful.

T. H. P.

**Derivatives of Gallic Acid. I. Synthesis of 4-Hydroxy-3:5-dimethoxyphthalic Acid.** RUPCHAND LILARAM ALIMCHANDANI and ANDREW NORMAN MELDRUM (T., 1920, 117, 964-970).

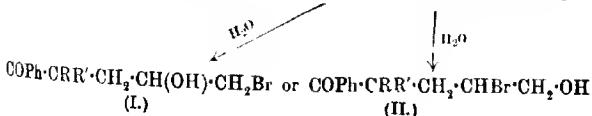
**Improved Process for the Elimination of Carboxyl Groups.** JAMES ERNEST MARSH (Brit. Pat. 144897).—Carboxyl groups may be eliminated from organic acids, particularly hydroxy-aromatic acids, such as gallic acid, by heating the acid with a dry metallic salt, preferably an alkali haloid. The reaction is advantageously carried out under reduced pressure, and, if the product is volatile, it may be conducted in a vacuum still, so that the decomposition of the acid and the recovery of the product by distillation proceed simultaneously. For instance, pyrogallol is obtained in a technically pure condition by distilling a mixture of gallic acid with half its weight of sodium chloride at 250° and 15 mm. pressure. The yield amounts to 95% of the theoretical.

G. F. M.

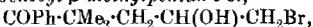
**Phenolphthalein.** F. URZ (Suddeut. Apoth. Zeit., 1920, 60, 430-431, 442-444; from Chem. Zentr., 1920, iv, 155).—The amounts of phenolphthalein in grams contained in 100 c.c. of a warm saturated solution of the substance in the various solvents are as follows: ethyl alcohol, 20.91; methyl alcohol, 14.18; acetone, 26.39; chloroform, 3.06; carbon disulphide, 0.18; ether, 5.92; light petroleum, 0.18 or 1.06, depending on the boiling point of the solvent; benzene, 0.16; carbon tetrachloride, traces; xylene, 0.18; toluene, 0.61; nitrobenzene, 4.41; ethyl acetate, 6.57. Water (10 c.c.) dissolves 0.0002 gram of phenolphthalein at the ordinary temperature, and about ten times this amount when warmed.

H. W.

**Bromohydrins and Dibromo-derivatives obtained from the Alkylallylacetophenones,  $\text{COPh}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ , and  $\text{COPh}\cdot\text{CRR}'\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ .** A. HALLER and (MME) P. RAVART-LUCAS (Compt. rend., 1920, 171, 144-148).—The dialkylacetophenones studied when treated with bromine in chloroform solution give bromohydrins, the intermediate dibromo-derivatives being unstable and decomposed by moisture. The authors favour the constitution (formula I) for the



bromohydrins obtained. Dimethylallylacetophenone in this way gives  $\epsilon$ -bromo- $\beta$ -benzoyl- $\beta$ -methylpentan- $\delta$ -ol,



m. p. 106°.

Diethylallylacetophenone gives  $\zeta$ -bromo- $\gamma$ -benzoyl- $\gamma$ -ethylhexan- $\delta$ -ol,  $\text{COPh}\cdot\text{C}(\text{Et}_2)\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$ , m. p. 84—88°.

Methylbenzylallylacetophenone gives  $\epsilon$ -bromo- $\beta$ -benzoyl- $\beta$ -benzylpentan- $\delta$ -ol,  $\text{COPh}\cdot\text{CMeBz}\cdot\text{CH}_2\cdot\text{CH}(\text{OII})\cdot\text{CH}_2\text{Br}$ .

Methylallylacetophenone under similar conditions gives a stable dibromo-derivative,  $\delta$ -dibromo- $\beta$ -benzoylpentane,



m. p. 128°.

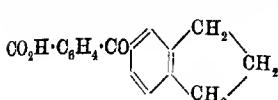
W. G.

**Benzo-polymethylene Compounds. I. Certain Regularities in Substitution.** JULIUS VON BRAUN, GEORG KIRSCHBAUM, and HANS SCHUHMANN (*Ber.*, 1920, **53**, [B], 1155—1173).—The communication is the first of a series devoted to the study of substances containing an aromatic nucleus to which a saturated hydrocarbon chain is cyclically attached. The action of oxalyl chloride, acetyl chloride, phthalic anhydride, and diethylmalonyl chloride on benzopentamethylene (hydrindene), tetrahydronaphthalene, and tetrahydroacenaphthene has been investigated. The behaviour of the first is not completely similar to that of either  $\alpha$ -xylene or naphthalene; tetrahydronaphthalene, in contrast to naphthalene, yields only uniform products instead of mixtures of isomerides, whilst tetrahydroacenaphthene gives a mixture of monobasic acids with oxalyl chloride.

Hydrindene and oxalyl chloride react in carbon disulphide solution in the presence of aluminium chloride to yield mainly hydrindene- $\beta$ -carboxylic acid, m. p. 178—179° (*chloride*, b. p. 140—142° 12 mm., *amide*, m. p. 137—138°), the constitution of which is deduced from its oxidation by nitric acid at 140° to trimellitic acid; hydrindene- $\alpha$ -carboxylic acid appears to be formed in small amount as by-product. Tetrahydronaphthalene and oxalyl chloride give exclusively tetrahydronaphthalene- $\beta$ -carboxylic acid, b. p. 216° 14 mm., m. p. 152—153°, which is readily hydrogenated by sodium and anil alcohol to decahydro-naphthalene- $\beta$ -carboxylic acid, b. p. 190—192°/21 mm., m. p. 79°. *Tetrahydronaphthalene- $\beta$ -carboxylic chloride* has b. p. 162°/13 mm., whilst the corresponding *amide* forms shining leaflets, m. p. 137—138°. Tetrahydroacenaphthene and oxalyl chloride yield a mixture of acids, which are separated by repeated crystallisation from alcohol; of these, the more sparingly soluble compound has m. p. 206° after softening at 200°, and is the main product. The *i*-isomeric acid has m. p. 170—180°, and has not been isolated in the pure state. Both isomerides yield benzene-1:2:3:4-tetracarboxylic acid when oxidised with nitric acid.

Acetyl chloride and hydrindene react readily, with formation of  $\beta$ -hydrindyl methyl ketone, b. p. 134—135°/11 mm. (*semicarb*—

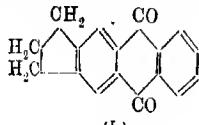
*uone*, m. p. 229°, *oxime*, m. p. 114°;  $\beta$ -hydrindyl bromomethyl ketone, leaflets, m. p. 58—59°, which do not attack the mucous membrane;  $\beta$ -hydrindyl dibromomethyl ketone, m. p. 58—59°. The  $\beta$ -position of the acetyl group follows from the oxidation of the ketone by permanganate to hydrindene- $\beta$ -carboxylic acid, and



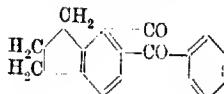
to an oily acid, which in all probability is  $\beta$ -hydrindoyl formic acid, and is oxidised by nitric acid to trimellitic acid. Hydrindene and phthalic anhydride give exclusively

$\beta$ -hydrindoylbenzoic acid (annexed formula), m. p. 169°, which is converted by zinc dust in ammoniacal solution into the acid,  $\text{CH}_2\begin{matrix} \text{CH}_2 \\ \text{CH}_2 \end{matrix}>\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. about 115°, but mainly

into the lactone,  $\text{CH}_2\begin{matrix} \text{CH}_2 \\ \text{CH}_2 \end{matrix}>\text{C}_6\text{H}_3\cdot\text{CH}\begin{matrix} \text{C}_6\text{H}_4 \\ \text{O} \end{matrix}>\text{CO}$ , m. p. 154°. It is decomposed with unusual difficulty by molten potassium hydroxide to yield hydrindene- $\beta$ -carboxylic acid. When dehydrated by fuming sulphuric acid, it gives a mixture of hydrindanthraquinones, delicate, matted needles, m. p. 180—181°, and yellow, crystalline powder, m. p. 108—110°. The formula



(I.)



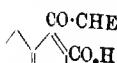
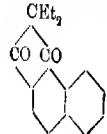
(II.)

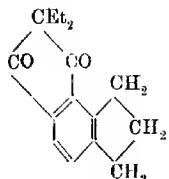
I and II are assigned to these respectively, since the former, on treatment with zinc and ammonia, gives hydrindanthraene, m. p.

242—243°, whilst the latter only yields readily soluble products of lower melting point, from which a definite substance could not be isolated.

Tetrahydronaphthalene and diethylmalonyl chloride yield exclusively the diethylindandione derivative (annexed formula), b. p. 207—211°, 15 mm., m. p. 56—57°, which is oxidised by nitric acid to benzene-1:2:3:4-tetra-carboxylic acid, m. p. 138°. Concentrated potassium hydroxide solution transforms the diketone into an acid, m. p. 135°, which probably has the annexed

constitution. Reduction of the diketone with amalgamated zinc and hydrochloric acid leads to the formation of the corresponding hydrocarbon, mobile oil, b. p. 164—166°/11 mm., which, however, is not completely free from oxygen; the latter can be totally eliminated by prolonging the duration of reduction, but, under these conditions, the hydrindene ring is ruptured, and the product is  $\gamma$ -methyl- $\gamma$ -

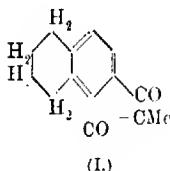




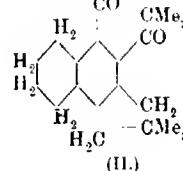
*ethylbutyltetrahydronaphthalene*, b. p. 141—144°/11 mm., which is oxidised by nitric acid to trimellitic acid. Diethylmalonyl chloride reacts with hydrindene in a precisely analogous manner, yielding the product (annexed formula), pale yellow, rather viscous oil, b. p. 186—191°/13 mm., which is oxidised by nitric acid to mellophanic acid, m. p. 238°. H. W. .

**Derivatives of *ac*-Tetrahydronaphthalene and of Tetrahydroacenaphthene.** KARL FLEISCHER and FRITZ SIEFERT (*Ber.*, 1920, **53**, [B], 1255—1261).—The action of substituted malonyl chlorides on partly hydrogenated aromatic hydrocarbons has been investigated by Fleischer (*Zeitsch. angew. Chem.*, 1919, **32**, [ii], 596; 1920, **33**, [ii], 160). Since the same subject is also engaging the attention of von Braun (preceding abstract), the authors give an account of their work with *ac*-tetrahydronaphthalene and tetrahydroacenaphthene, but reserve the full experimental details for a later publication.

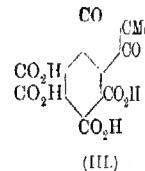
Dimethylmalonyl chloride and tetrahydronaphthalene yield exclusively 2:2-dimethyltetrahydronaphth- $\alpha\beta$ -indane-1:3-dione (I), m. p. 75°, which is hydrolysed to 1-isobutyryltetrahydronaphthalene-2-carboxylic acid, m. p. 120°; the latter is oxidised by nitric acid to 2:2-dimethylbenzindane-1:3-dione 6:7-dicarboxylic acid. The indanone is reduced by amalgamated zinc and hydrochloric acid to 2:2-dimethyltetrahydronaphth- $\alpha\beta$ -hydrindene, b. p. 156°/18 mm. The  $\alpha\beta$ -position of the hydrindene ring in the hydrocarbon molecule is established by its conversion by dimethylmalonyl chloride into 2:2:5:5-tetramethyltetrahydronaphthidihydrindene-4:6-dione (II), m. p. 118—149°, which is reduced to 2:2:5:5-tetramethyltetrahydronaphthidihydrindene, m. p. 105—106°, and is oxidised by nitric acid to a tetracarboxylic acid (III), decomposing at 277°, and mellitic acid.



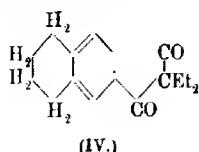
(I.)



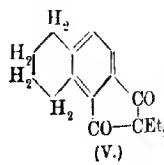
(II.)



(III.)



(IV.)



(V.)

With diethylmalonyl chloride and tetrahydronaphthalene, both isomerides are formed; *2:2-diethyltetrahydronaphth-ββ-indane-1:3-dione* (IV) has m. p. 118°, whilst *2:2-diethyltetrahydronaphth-αβ-indane-1:3-dione* (V) has m. p. 54–55°. Only the second of these yielded a well-defined *acid*, m. p. 134–135°, on hydrolysis. The former dione is oxidised by nitric acid to pyromellitic acid, whilst the latter gives *2:2-diethylbenzindane-1:3-dione-6:7-dicarboxylic acid*, m. p. 174–176°. The diones are completely reduced by amalgamated zinc and hydrochloric acid to *2:2-diethyltetrahydronaphth-αβ-hydridene*, m. p. 49°, and *2:2-diethyltetrahydronaphth-αβ-hydridene*, b. p. 163–165°/12 mm., respectively.

[With WILHELM ECKERT.]—*2-Acetyltetrahydronaphthalene* is reduced to *2-ethyltetrahydronaphthalene*, b. p. 127°/21 mm., from which, by regulated acetylation and subsequent reduction, *2:3-diethyltetrahydronaphthalene*, b. p. 150–151°/18 mm., and *1:2:3-triethyltetrahydronaphthalene*, b. p. 165–172°/23 mm., are successively prepared.

Tetrahydroacenaphthene is transformed by diethylmalonyl chloride into *2:2-diethyltetrahydronaphth-αβ-indane-1:3-dione* (annexed formula), m. p. 88–89°, which is reduced by amalgamated zinc and hydrochloric acid to *2:2-diethyltetrahydronaphth-αβ-hydridene*, b. p. 190–195°/16 mm. The dione is oxidised to a mixture of benzenepentacarboxylic acid and *diethylbenzindane-1:3-dione 4:5:6-tricarboxylic acid*. H. W.

**Menthyl and Phenylhydrazine Derivatives of the Higher Fatty Acids.** D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1920, **42**, 1478–1481).—The menthyl esters and phenylhydrazine derivatives of certain of the higher fatty acids were prepared in an attempt to find a means of estimating the amounts of individual acids present in mixtures. This aim was not fulfilled. The menthyl esters prepared by heating the acid chlorides with menthol were *menthyl laurate*,  $D_4^{20}$  0.8915,  $[\alpha]_D^{20}$  –46°7 $^2$ ; *menthyl myristate*, n. p. 21–22°,  $D_4^{20}$  0.882,  $[\alpha]_D^{20}$  –42.3 $^2$  (compare Hilditch, T., 1912, **101**, 192); *menthyl palmitate*, m. p. 32°,  $D_4^{20}$  0.8848,  $[\alpha]_D^{20}$  –39.6 $^2$ ; *menthyl stearate*, m. p. 38–39°,  $D_4^{20}$  0.8665,  $[\alpha]_D^{20}$  –36.6 $^2$ ; *menthyl arachidate*, m. p. 55°,  $D_4^{20}$  0.8568,  $[\alpha]_D^{20}$  –30.63°. All these rotations were determined directly on the molten substances. The phenylhydrazides, prepared by heating the acids with excess of phenylhydrazine, were *palmitic phenylhydrazide*, m. p. 105°; *stearic phenylhydrazide*, m. p. 110–111°; *arachidic phenylhydrazide*, m. p. 108–109°. W. G.

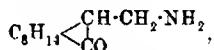
**"Cresineol," a Compound of Cineole and *o*-Cresol.** T. TUNSTING COCKING (*Pharm. J.*, 1920, **105**, 81).—When one molecule of cineole is mixed with one molecule of *o*-cresol, heat is developed, and a crystalline substance separates as the mixture

cools. The name "cresineol" is given to the substance. It has m. p. 55.2°, b. p. 186.5—189°,  $D_4^{20}$  0.9661, and  $n_D^{20}$  1.4846; it is soluble in most organic solvents, and is decomposed by alkali hydroxides into its constituents.

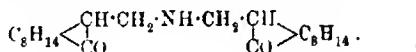
W. P. S.

**Dependence of Optical Rotatory Power on Chemical Constitution. II. The Effect of Position-isomerism and Conjugation on Optical Activity among Aryl Derivatives of Amino- and Bisimino-camphor.** BAWA KARTAR SINGH, DALIP SINGH, GURU DUTT, and COPAL SINGH (T., 1920, 117, 980—988).

**Reduction Products of Hydroxymethylenecamphor. IV. Coupling of Bases with Methylenecamphor.** HANS RUPE and WALTER KUSSMAUL (*Helv. Chim. Acta*, 1920, 3, 515—540. Compare A., 1919, i, 335).—Unsuccessful attempts have been made to prepare the methylecamphoramine of the structure,

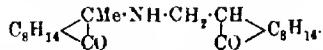


(1) by treating camphylbromomethane with ammonia, and (2) by reduction of aminomethylenecamphor. Reaction (1) yields a compound which forms a nitrosoamine, a benzoyl derivative and a phenylthiocarbamide derivative, and may be obtained also by reduction with aluminium amalgam in neutral solution of the imide described by Bishop, Claisen, and Sinclair (A., 1895, i, 62); this compound is evidently di(camphomethyl)-amine,



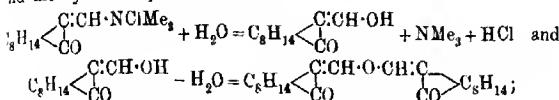
The latter is obtained also when methylenecamphor is treated with ammonia in a sealed tube, and when camphylcarbinol and ammonia react under pressure. Derivatives of the methylcamphoramine sought may, however, be obtained. Thus, the action of diethylamine on methylenecamphor gives diethylcamphomethylamine,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH} \cdot \text{CH}_2 \cdot \text{NEI}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ , which is obtainable also from camphylbromomethane and diethylamine.

Reduction of aminomethylenecamphor by means of aluminium amalgam gives in small yield a base which is isomeric with, and exhibits quite similar behaviour to, the secondary base obtained by reaction (1), and is probably of the structure



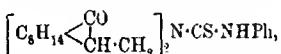
Attempts were also made to prepare the desired methylcamphoramine by reducing methylenecamphoramide with hydrogen in presence of nickel, by means of camphylbromomethane and phthalimide, and from the amide of camphorylacetic acid (compare Rupe, Warder, and Takagi, A., 1919, i, 27), but in no case successfully.

Various quaternary ammonium compounds derived from ethylene- and methyl-camphor are described. Noteworthy is the formation of the anhydride of hydroxymethylenecamphor (compare Bishop, Claisen, and Sinclair, *loc. cit.*) by treatment with sodium hydroxide of the quaternary base obtained from trimethylamine and methylenecamphor chloride:



The trimethylamine liberated acts as the dehydrating agent.

*Di(camphomethyl)-amine*,  $(\text{C}_{11}\text{H}_{17}\text{O})_2\text{NH}$ , forms an amorphous, crumbly, white mass of faintly basic odour, m. p.  $124^\circ$ , and decomposes on distillation even under reduced pressure. The *hydrobromide*,  $(\text{C}_{11}\text{H}_{17}\text{O})_2\text{NH}\cdot\text{HBr}$ , slender, white leaflets, sintering and blackening at  $285^\circ$ , and remaining unmelted at  $350^\circ$ ; the *hydrochloride*, thin, white leaflets or felted needles with a persistent, bitter taste, sintering and blackening at  $270^\circ$ , and remaining unmelted at  $350^\circ$ ; the *platinichloride*, quadratic leaflets, boiling suddenly and blackening at  $240^\circ$ ; the *oxalate* (normal), microscopic, rectangular leaflets, decomposing at  $191-192^\circ$ ; the *nitrosoamine*,  $\text{C}_8\text{H}_{14} < \text{CO} \begin{array}{c} \text{CH}\cdot\text{CH}_2\text{N}(\text{NO})\cdot\text{CH}_2\cdot\text{CH} \\ | \\ \text{CO} \end{array} > \text{C}_8\text{H}_{14}$ , slender, white needles, softening at  $100^\circ$ , m. p.  $106^\circ$ ; and the *benzyl derivative*,  $\text{C}_{20}\text{H}_{30}\text{O}_3\text{N}$ , bundles of slender needles, m. p.  $132^\circ$ , were prepared. *Di(camphomethyl)-phenylthiocarbamide*,



forms slender, silky needles, m. p.  $160-161^\circ$ , and is sometimes accompanied by an *isomeride*, m. p.  $129-130^\circ$ .

The base,  $\text{C}_{22}\text{H}_{38}\text{O}_2\text{N}$ , obtained by reducing aminomethylenecamphor by means of aluminium amalgam, forms a friable mass, softening at  $130^\circ$ , m. p.  $145-146^\circ$ . The following derivatives were prepared: *hydrochloride*, slender, rectangular leaflets, neither melting nor decomposing; *platinichloride*, decomposing at  $230^\circ$ ; *oxalate*, glittering leaflets, softening at  $250^\circ$ , m. p.  $258^\circ$  (decomp.); *nitrosoamine*,  $\text{C}_{22}\text{H}_{34}\text{O}_3\text{N}_2$ , crystalline powder, softening at  $158^\circ$ , m. p.  $164^\circ$ .

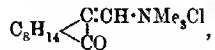
Reduction of methylenecamphorimide by means of aluminium amalgam yields methylenecamphor, *di(camphomethyl)-amine*, and a base, giving an oxalate, m. p.  $248-250^\circ$ .

Similar reduction of ethyl methyleucamphor-*p*-aminobenzoate yields ethyl *p*-aminobenzoate, together with a compound,  $\text{C}_8\text{H}_{22}\text{O}_3\text{N}$  or  $\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}$ , crystallising in small prisms, m. p.  $178-179^\circ$ .

*Diethylcamphomethylamine*,  $\text{C}_{15}\text{H}_{27}\text{ON}$ , is a pale yellow, oily liquid of faintly basic odour, b. p.  $137.5^\circ/8.5 \text{ mm}$ . The *hydrochloride*, slender, white needles, m. p.  $167-168.5^\circ$ , giving a bitter,

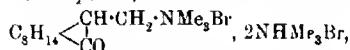
aqueous solution, and the *platinichloride*, slender, salmon-coloured needles, m. p. 194°, decomposing at 212°, were prepared.

*Methylenecamphortrimethylammonium chloride*,



prepared from methylenecamphor chloride and trimethylamine, forms vitreous, quadratic, deliquescent plates, m. p. 162°, and yields intensely bitter, aqueous solutions. With sodium hydroxide, the aqueous solution of the chloride yields trimethylamine, and, on subsequent acidification, hydroxymethylenecamphor; when heated in a reflux apparatus on a boiling-water bath, it gives the anhydride of hydroxymethylenecamphor.

Methyleamphortrimethylammonium chloride could not be prepared, but the corresponding bromide, obtained from camphor, bromomethane and trimethylamine, forms with trimethylamine hydrobromide the compound,



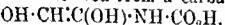
which crystallises in colourless leaflets, softening at 183°, melting at 192°, again solidifying and melting a second time, and boiling at 280°. T. H. P.

**Essential Oil of *Mosta grosseserrata*, Maxim.** YOSHIAKU MURAYAMA (*J. Pharm. Soc. Japan*, 1920, 389-408. Compare Furukawa and Tomizawa, *J. Chem. Ind. Japan*, 1919, **22**, 383). Three specimens of the essential oil from the wild plant contained: (1) thymol, methyleugenol, *p*-cymene, a terpene, and a sesquiterpene, b. p. 136°, 12 mm.; (2) thymoquinol; (3) myristicin. The oil from the cultivated plant contained thymoquinol, thymol, and a terpene. K. K.

**Hiptagin, a New Glucoside from *Hiptage madabola*, Gaertt.** K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], 2, 187-202). This glucoside is extracted in a yield of 8% from the root bark by acetone or ethyl acetate. The bark of the stem contains much less. *Hiptagin*,  $\text{C}_{19}\text{H}_{14}\text{O}_4\text{N}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , forms silky needles, m. p. 110°,  $[\alpha]_D -3.5^\circ$  in 5% acetone solution. The most characteristic chemical property is the formation by dilute alkali hydroxide, even in the cold, of ammonia and hydrocyanic acid. Dilute acids act quite differently, forming dextrose, and, at the same time, breaking down the genin in various ways; 5% aqueous sulphuric acid at 100° forms tartronic acid. Concentrated hydrochloric acid, mixed with 4 volumes of acetone, forms in five days at the ordinary temperature strong, monobasic *hiptagenic acid*,  $\text{C}_3\text{H}_4\text{O}_4\text{N}$ , needles, m. p. 68°,  $k = 1.20 \times 10^{-4}$ , giving crystalline silver, lead, and zinc salts. The hypothetical hiptagenin is decomposed according to the equation  $\text{C}_1\text{H}_4\text{O}_4\text{N}_2 + 2\text{H}_2\text{O} = \text{C}_3\text{H}_4\text{O}_4\text{N} + \text{CO}_2 + \text{NH}_3$ . *Hiptagenic acid* is also formed by destructive distillation of the glucoside, and is regarded as having the constitution  $\text{OH} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}(\text{OH}) \cdot \text{CH} \cdot \text{OH}$ . By heating *hiptagenic acid*

with hydrochloric acid on the water-bath, it is hydrolysed to diglycolic and formic acids and to hydroxylamine hydrochloride,  $C_3H_5O_4N + 3H_2O = C_4H_6O_5 + 2HCO_2H + 2NH_2OH$ . Sodium ethoxide at the ordinary temperature decomposes hiptagin, with the formation of sodium nitrite, but hiptagenic acid is only slowly hydrolysed by boiling alcoholic sodium ethoxide solution, probably with the formation of formhydroxamic acid (red coloration with ferric chloride) and of glyoxal,  $OH\cdot CH\cdot C(OH)\cdot CO\cdot NH\cdot OH = OH\cdot CH\cdot N\cdot OH + CHO\cdot CHO$ . The action of aqueous alkalis on hiptagenic acid is very complex. The best results were obtained by heating with barium hydroxide at  $50^\circ$ , which formed barium nitrite, barium formhydroxamate, and (in 72% yield) a salt,  $C_3H_5O_4NBa$ .

The latter is regarded as derived from a carbamic acid,



isomeric with hiptagenic acid. On heating with phosphoric acid, the barium salt gives half a molecular proportion of carbon dioxide, hydrocyanic and oxalic acids, ammonia, formaldehyde, and glyoxal. The isomerisation of hiptagenic to the carbamic acid is compared to the Beckmann transformation of oximes. The carbamic acid may be decomposed on the one hand to ammonia and glyoxal, and on the other to formaldehyde, water, and cyanoformic acid. The last-named may yield hydrocyanic acid and carbon dioxide, or oxalic acid and ammonia. Glyoxal and formaldehyde were obtained as *p*-nitrophenylhydrazones.

The action of barium hydroxide on hiptagin takes place according to the equation  $C_{10}H_{14}O_9N_2 + 3H_2O = C_6H_{12}O_6 + C_3H_5O_4N + CO_2 + NH_3$ . The barium salt of the carbamic acid here has the composition  $(C_3H_5O_4N)_2Ba$ , and appears to

$C_6H_{11}O_2\cdot C\begin{cases} H \\ | \\ OH \end{cases} - \begin{cases} H \\ | \\ NH \end{cases} - CO - C\begin{cases} H \\ | \\ N \\ \backslash \\ O \end{cases}$  be derived from the tautomeric form,  
 $CHO\cdot CH(OH)\cdot NH\cdot CO_2H$ ,  
without the two acid hydroxymethylene groups formulated above for the salt from hiptagenic acid. The author proposes for

hiptagin the annexed formula of an *isooxazole* derivative. He considers that it is formed in the plant by reduction of nitrates to hydroxylamine, and condensation of this base with aldehydes and ketones.

G. B.

**Synthesis of Aromatic Amino-acids in the Living Cell.**  
L. HUGOUNENQ and GABRIEL FLORENCE (*Bull. Soc. chim. Biol.*, 1920, **2**, 133-136).—Aspergillin, the black pigment of *Aspergillus niger*, previously described by Linossier (A., 1891, 751, 1039), is prepared by extracting the spores with cold 10% sodium hydroxide. The extract, on being neutralised with sulphuric acid, produces a flocculent, black precipitate of the pigment in a more or less pure condition. After purification, the product forms a shining, amorphous powder, insoluble in water and in acids, but very soluble in alkalis. It contains 4.97% of ash, in which were present iron, sulphur, zinc, and calcium. Elementary analysis gave the percentage figures: C 43.5, H 6.9, N 12.6, P 8.7, Fe 0.455,

b b\* 2

Ca 0.352, Mg 0.126, S 0.57, O 27.367. It appears to contain an indole ring in the molecule. J. C. D.

**Henna (Lawsonia inermis). Chemical Constitution of Lawsone. II.** G. TOMMASI (*Gazzetta*, 1920, **50**, i, 263—272).—Lawsone, the colouring matter contained in henna leaves (compare *Ann. R. Staz. Chim. agr. sper. Roma*, 1920, **10**), forms crystals, m. p. 192—195° (decomp.), and gives an orange-yellow, aqueous solution, which undergoes change when boiled. It is fixed well by wool and silk, and, rapidly and tenaciously, by the skin. In aqueous solutions of alkali or alkaline earth hydroxides, or in concentrated sulphuric acid, it dissolves, giving a bright orange-red coloration. In aqueous-alcoholic solution it gives: with ferric chloride, a reddish-brown precipitate; with stannous chloride or alum, a yellow precipitate; with copper acetate, an orange precipitate; with silver nitrate, an orange-red precipitate; with tannin it remains unchanged.

Its composition and its ebullioscopic behaviour in alcohol indicate the formula  $C_{10}H_6O_3$ , and it is distinctly acid in character and contains no methoxyl groups. The calcium salt,  $Ca(C_{10}H_6O_3)_2$ , forms silky, red needles. The *acetyl* derivative,  $C_{10}H_6O_2OAc$ , crystallises in shining needles, m. p. 128—130°. When reduced by means of zinc dust and acetic acid, it is converted into a colourless leuco-derivative, which is readily oxidised to the original compound by atmospheric oxygen. By treatment with acetic anhydride and zinc dust, it is transformed into the compound,  $C_{10}H_4O_6$ , which crystallises in nacreous, white laminae, m. p. 133—134°. The conclusion is drawn that the molecule of lawsone contains one phenolic hydroxyl oxygen atom and two quinonic oxygen atoms. Further, since, in alcoholic solution, lawsone gives with nickel acetate an intense red coloration, and after some hours a deposit of garnet-red crystals (compare Brissemoret and Combes, A., 1907, ii, 411), the substance must be regarded as a hydroxy-naphthaquinone, and is probably identical with 2-hydroxy-1:4-naphthaquinone.

T. H. P.

**Formation of Melanin.** J. VERNE (*Compt. rend. Soc. Biol.*, 1920, **83**, 760—762; from *Chem. Zentr.*, 1920, iii, 156).—The brown dye, which has been proved histologically to be converted into melanin, is completely soluble in warm water, alkaline and acid solutions, and in formalin, but quite insoluble in alcohol and solvents for fats. The aqueous solution is faintly acidic, does not give the biuret or purine reactions, dissolves cupric hydroxide, and is readily diazotised. Addition of neutral formalin renders the solution strongly acidic. Addition of solutions of tyrosinase causes rapid blackening. Millon's reaction is strongly marked. The dye consists of polypeptides in which tyrosine is present, and is classed as an amino-acid dye. A considerable portion of the nitrogen, which can be titrated with formalin, disappears during the formation of melanin, whilst the total nitrogen remains unchanged.

H. W.

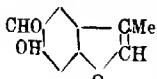
**The Constitution of Catechin. I. MAXIMILIAN NIRRENSTEIN**  
(T., 1920, 117, 971—979).

**Syntheses in the Bergaptene Group.** P. KAREER, A. GLATTFELDER, and FR. WIDMER (*Helv. Chim. Acta*, 1920, **3**, 541—558).—Condensation of 5-hydroxy-2-methylcoumarone with hydrocyanic acid and hydrogen chloride yields 5-hydroxy-2-methylcoumarone-4-aldimide hydrochloride, and the latter, when boiled with water, yields an aldehyde which is to be investigated later, but is most probably 5-hydroxy-2-methylcoumarone-4-aldehyde. When heated with acetic anhydride and sodium acetate, this aldehyde yields an “intermediate compound,” which is converted when boiled with distilled water into 5-hydroxy-2-methylcoumarone-4-acrylic acid; treatment of the latter with methyl sulphate in concentrated alkaline solution yields 5-methoxy-2-methylcoumarone-4-acrylic acid, whilst in faintly alkaline solution methyl 5-methoxy-2-methylcoumarone-4-acrylate is obtained. The acrylic acid is highly stable, and shows not the slightest tendency to undergo dehydration to the corresponding coumarin; similarly, 5-hydroxy-4-chloroacetyl-2-methylcoumarone exhibits no tendency to ring-formation with loss of hydrogen chloride, the phenomenon in both cases being probably due to steric hindrance.

In order to exclude the influence of the methyl group of the furan ring and to approach more closely to the natural products, bergaptene and xanthotoxin, coumarone-coumarin derivatives free from methyl groups have been prepared. 5-Hydroxycoumarone is obtainable with difficulty from 7-acetoxycoumarin (compare Pechmann, A., 1884, 1173) by way of the dibromide and 5-hydroxycoumarone-1-carboxylic acid. 5-Hydroxycoumarone reacts with hydrocyanic acid and hydrogen chloride, giving 5-hydroxycoumarone-4-aldimide hydrochloride, which is converted on hydrolysis with hot water into 5-hydroxycoumarone-4-aldehyde. Like the methylated compounds mentioned above, this aldehyde is not converted into the coumarin expected when boiled with acetic anhydride and sodium acetate.

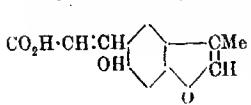
The methyl ether of phloroglucinol undergoes condensation with ethyl acetoacetate and sodium, yielding an ethyl methoxyhydroxy-methylcoumaronecarboxylate. Cautious sublimation of the corresponding free acid gives the methoxymethylcoumarone, in which the closure of the coumarone ring takes place in either the ortho- or the para-position to the methoxyl group of the benzene nucleus.

*5-Hydroxy-2-methylcoumarone-4-aldehyde* (annexed formula), crystallises in pale yellow needles, m. p. 181°, and in alcoholic solution gives a green coloration with ferro chloride. The *oxime*,  $C_{16}H_{18}O_3N$ , forms long, white needles, m. p. 186° (decomp.), the *anil*,  $C_{16}H_{18}O_2N$ , yellow or yellowish-brown needles, m. p. 160° (decomp.), and the *phenylhydrazone*, yellow crystals, m. p. 165° (decomp.).



The intermediate compound (see above) forms small, yellow crystals, m. p.  $114^{\circ}$ , and is insoluble in sodium carbonate, hydrogen carbonate, or hydroxide solution.

*5-Hydroxy-2-methylcoumarone-4-acrylic acid (annexed formula)*

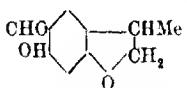


one-4-acrylic acid (annexed formula) crystallises in shining, pale yellow needles, m. p. 199°, sublimes partly at a higher temperature, dissolves readily in alkali solutions, and in acetone solution decolorises permanganate.

### 5 - Methoxy - 2 - methylcoumarin-1.

*acrylic acid*,  $C_{13}H_{12}O_4$ , forms pale yellow needles, m. p.  $209^\circ$ , and dissolves readily in alkali solution. Its *methyl ester*,  $C_{14}H_{14}O_4$ , crystallises in yellow needles, m. p.  $216^\circ$ .

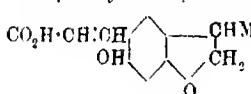
*5-Hydroxy-2-methylcoumaran-4-aldehyde* (annexed formula), pre-



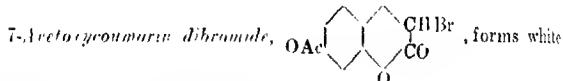
pared by the action of boiling water on the aldimide hydrochloride obtained by condensing  $\delta$ -hydroxy-2-methylcoumaran (A, 1919, i, 595) with hydrocyanic acid and hydrogen chloride, crystallises in needles, m. p. 185°. The orime,  $C_{10}H_{11}O_3$ , m. p. and the hydrochloride were prepared

190° (decomp.), the anil, and the hydrazone were prepared.

**5-Hydroxy-2-methylcoumaran-4-acrylic acid (annexed formula).**

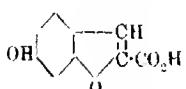


prepared by boiling the preceding compound with acetic anhydride and sodium acetate, crystallizes in pale yellow needles, m. p. 208°. In this case also no compound of  $\alpha$  obtained.



leaflets, in, p. 114° (frothing).

### 5-Hydroxyguanidine-1-carboxylic acid (5-hydroxyguanidine-



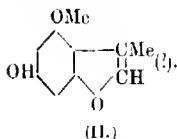
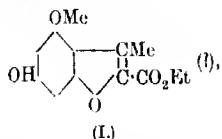
and) (annexed formula), prepared by the action of alcoholic potassium hydroxide on the preceding compound, crystallises in microscopic leaflets, m. p. 234°-236° (uncorr.) (decomp.), gives a brown coloration in alcoholic solution with ferric chloride.

and dissolves in aqueous alkali to a solution showing blue fluorescence, which disappears when the liquid is boiled.

5-Hydroxycoumarone, obtained by rapid distillation of 5-hydroxycoumaric acid with calcium oxide, forms long, flat needles, m. p. 56°, dissolves readily in alkali solution, quickly decolorises permanganate in acetone solution, gives a green coloration in alcoholic solution with ferric chloride, and is resupplied with a red coloration by concentrated sulphuric acid.

5-Hydroxycoumarone-4-aldehyde (annexed formula) forms white crystals, decomposes without melting at 260°, and in alcoholic solution gives a canary-yellow coloration with aniline hydrochloride. When boiled with acetic anhydride and sodium acetate it yields a compound which has not the composition of a simple coumarone-coumarin.

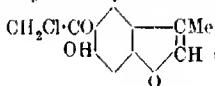
Ethyl hydroxymethoxymethylcoumaronecarboxylate (I), forms



crystals, m. p. 230°. The corresponding acid forms a white precipitate, m. p. 202° (decomp.).

Hydroxymethoxymethylcoumarone (II) is obtained as a white sublimate, m. p. 75° (previous softening), and has the odour of coumarone.

5-Hydroxy-4-chloroacetyl-2-methylcoumarone,



obtained from 5-hydroxy-2-methylcoumarone and chloroacetonitrile, forms crystals, m. p. 192°, and dissolves readily in dilute sodium hydroxide solution.

T. H. P.

3:6-Tetramethyldiaminoselenopyronine. M. BATTEGAY and G. HÜGEL (*Bull. Soc. chim.*, 1920, [iv]. 27, 557—560).—A mixture of sodium selenite and sulphuric acid is added gradually to sulphuric acid containing 25% of sulphur trioxide and at the same time tetramethyldiaminodiphenylmethane is added in small portions, so that it is always present in slight excess, the temperature not being allowed to rise above 35°. After an hour and a-half the mixture is poured on to ice, filtered, and a solution of zinc chloride added to the filtrate. The zincchloride of tetramethyldiamino-selenopyronine,  $C_{15}H_{19}N_2Cl_2Se.ZnCl_2$ , is obtained in a crystalline form. It dissolves in sulphuric acid to a red solution, which on dilution with water turns blue. The addition of sodium hydroxide to this solution precipitates a reddish-blue base, which is soluble in ether. The colouring matter gives slightly soluble iodides and nitrates and insoluble dichromates.

W. G.

Synthesis of Derivatives of 1:3-Oxthiophan. A. BISTRZYCKI and BRUNO BRENNEN (*Helv. Chim. Acta*, 1920, **3**, 447—467).—The behaviour of thiobenzyllic acid ( $\alpha$ -mercaptodiphenylacetic acid) (com-

pare Becker and Bistrzicki, A., 1915, i, 245) towards aldehydes, ketones, and ketonic acids is found to be analogous to that of thioglycolic acid (Bongartz, A., 1886, 937; 1888, 478) and  $\alpha$ -thiolactic acid (Holmberg and Mattisson, A., 1907, i, 475) towards these carbonylic compounds.

*4:4-Diphenyl-1:3-oxithiophan-5-one* (methylene ether ester of thiobenzyllic acid),  $\text{CPh}_2\begin{array}{c} \text{S}-\text{CH}_2 \\ \swarrow \quad \searrow \\ \text{CO} \quad \text{O} \end{array}$ , prepared by the interaction of formaldehyde and thiobenzyllic acid, crystallises in flat prisms or rhombic or triangular plates, m. p. 99–100°. Alkali carbonate or hydroxide decomposes it with formation of thiobenzyllic acid, whilst with ammonia solution it yields diphenylacetamide and diphenylacetic acid. It is not changed by concentrated hydrochloric acid at 100°, but dissolves gradually in concentrated sulphuric acid to a yellow solution, which becomes deep violet after a few minutes or more rapidly on heating. It is not attacked by bromine in boiling chloroform solution. By zinc dust and boiling acetic acid it is decomposed, yielding thioformaldehyde (?) and diphenylacetic acid, whilst chromic anhydride in acetic acid converts it into

*4:4-Diphenyl-1:3-orthiophan-5-one-3-dioxide*,  $\text{CPh}_2\begin{array}{c} \text{SO}_2\text{CH}_2 \\ \swarrow \quad \searrow \\ \text{CO} \quad \text{O} \end{array}$ ,

which crystallises in glistening quadrilateral leaflets or flat prisms, m. p. 92–94°, and with concentrated sulphuric acid yields a cupric blue solution deepening considerably in colour when heated. When a solution of the sulphone in dilute, boiling alkali hydroxide is rendered acid with hydrochloric acid, it yields sulphur dioxide and a white, flocculent precipitate.

*4:4-Diphenyl-2-methyl-1:3-orthiophan-5-one*,  $\text{CPh}_2\begin{array}{c} \text{S}-\text{CHMe} \\ \swarrow \quad \searrow \\ \text{CO} \quad \text{O} \end{array}$ ,

prepared from acetaldehyde and thiobenzyllic acid, forms microscopic, colourless, four-sided plates, often in bundles, m. p. 89–91°, and behaves towards concentrated sulphuric acid similarly to its lower homologue.

*4:4-Diphenyl-2-methyl-1:3-oxithiophan-5-one-3-dioxide*.

$\text{CPh}_2\begin{array}{c} \text{SO}_2\text{CHMe} \\ \swarrow \quad \searrow \\ \text{CO} \quad \text{O} \end{array}$ ,

obtained on oxidising the preceding compound, exists in two modifications, which are possibly stereoisomerides related in the manner indicated by Hinsberg (A., 1916, i, 725; 1917, ii, 173, 461). The  $\alpha$ -form crystallises in colourless plates, m. p. 79–81°, and dissolves in hot concentrated sulphuric acid with formation of a reddish-brown solution with a violet reflexion. The  $\beta$ -form, obtained along with the  $\alpha$ -form or by treating the latter with boiling acetic acid, crystallises in colourless, microscopic rhombohedra, m. p. 97–99°.

*4:4-Diphenyl-2-trichloromethyl-1:3-oxithiophan-5-one*.

$\text{CPh}_2\begin{array}{c} \text{S}-\text{CH}\cdot\text{CCl}_3 \\ \swarrow \quad \searrow \\ \text{CO} \quad \text{O} \end{array}$ ,

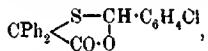
prepared from chloral and thiobenzyllic acid, forms colourless, pris-

natic plates, m. p. 107°. In hot concentrated sulphuric acid it dissolves with emission of an intense garlic odour and formation of a violet solution, turning first blue and then an indistinct green.

2:4:4-Triphenyl-1:3-oxthiophan-5-one,  $\text{CPh}_2\text{---}\begin{matrix} \text{S---CHPh} \\ \text{CO---O} \end{matrix}$ , obtained from benzaldehyde and thiobenzylic acid, forms colourless, mostly hexagonal plates, m. p. 94—96°. With ammonia solution at 125° it gives a small yield of a compound, m. p. 163—165°, of unknown character. It is not attacked by concentrated hydrochloric acid at 100°, but with aniline it furnishes an additive compound,  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{S}_2\text{NH}_2\text{Ph}$ , which crystallises in bundles of colourless plates, softening at 67°, then gradually melting and giving a clear liquid only at 77.5°. It is not changed at 100° by methyl iodide in presence or absence of methyl alcohol, but undergoes profound decomposition when boiled with a chloroform solution of bromine. With concentrated sulphuric acid it gives a yellow solution, quickly becoming violet-red with slight evolution of gas.

2:4:4-Triphenyl-1:3-oxthiophan-5-one-3-oxide,  $\text{CPh}_2\text{---}\begin{matrix} \text{SO---CHPh} \\ \text{CO---O} \end{matrix}$ , obtained by oxidising the preceding compound, crystallises in microscopic prisms, often united in bundles, m. p. 158.5—160.5°, and in concentrated sulphuric acid yields a greenish-yellow solution becoming violet-brown when heated. When boiled with normal potassium hydroxide solution, it emits an odour of benzaldehyde.

4:4-Diphenyl-2-p-chlorophenyl-1:3-oxthiophan-5-one,



obtained from *p*-chlorobenzaldehyde, crystallises in slender, silky prisms or concentric aggregates of colourless, four-sided prisms, m. p. 125—126°, and towards concentrated sulphuric acid behaves like the chlorine-free compound.

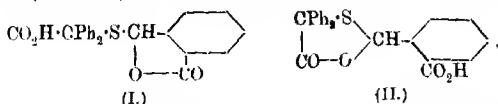
4:4-Diphenyl-2-*o*-nitrophenyl-1:3-oxthiophan-5-one,  $\text{C}_{21}\text{H}_{15}\text{O}_4\text{NS}$ , from *o*-nitrobenzaldehyde, forms colourless, four-sided plates, m. p. 116.5—117.5°, and gives a violet-brown solution in concentrated sulphuric acid.

4:4-Diphenyl-2-*m*-nitrophenyl-1:3-oxthiophan-5-one,  $\text{C}_{21}\text{H}_{15}\text{O}_4\text{NS}$ , from *m*-nitrobenzaldehyde, forms iridescent, white, quadrilateral plates, m. p. 132—133°.

4:4-Diphenyl-2-*o*-hydroxyphenyl-1:3-oxthiophan-5-one,  $\text{C}_{21}\text{H}_{16}\text{O}_3\text{S}$ , formed from salicylaldehyde, crystallises in colourless, microscopic rhombs, m. p. 147° (decomp.), and dissolves in concentrated sulphuric acid to a greenish-orange solution, becoming violet-brown when heated. In ammonia solution it gives a greenish-yellow solution, and in normal potassium hydroxide a greenish-brown solution which soon loses its colour. Its acetyl derivative,  $\text{C}_{22}\text{H}_{16}\text{O}_4\text{S}$ , forms flat prisms or concentric aggregates of microscopic, rhombic plates, m. p. 104—105°.

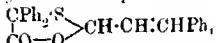
4:4-Diphenyl-2-p-anisyl-1:3-oxathiophan-5-one,  $C_{22}H_{18}O_3S$ , obtained from anisaldehyde, forms colourless, microscopic plates or heavy plates, m. p. 103–104°, and dissolves in concentrated sulphuric acid to a greenish-yellow solution, rapidly turning orange-brown.

The  $\gamma$ -lactone (I), or, possibly, (II), obtained from *o*-phthalaldehyde.



hydric acid and thiobenzylic acid, crystallises in microscopic, four-sided plates, turns blue at 150°, and decomposes at 168°; it forms also the hydrate,  $+H_2O$ , which softens at 115°. It dissolves in concentrated sulphuric acid, giving a yellowish-brown solution, quickly turning brownish-red with a violet tinge. Its *barium* salt was prepared and analysed.

4:4-Diphenyl-2-styryl-1:3-oxathiophan-5-one,



obtained from cinnamaldehyde, forms microscopic, colourless, pointed, rhombic plates, m. p. 156–157° (decomp.); its solution in concentrated sulphuric acid is orange-coloured, and slowly becomes brown or, when heated, brownish-red.

4:4-Diphenyl-2:2-dimethyl-1:3-oxathiophan-5-one,  $\text{CPh}_2\text{S}$   
 $\text{CO}-\text{O}-\text{CMe}_2$

obtained from acetone and thiobenzylic acid, forms flat, white prisms, m. p. 119.5–120.5°, gives a brownish-red solution with a violet tinge in concentrated sulphuric acid, and is decomposed into its components when boiled with alcoholic potassium hydroxide solution.

2-Carbonyl-4:4-diphenyl-2-methyl-1:3-*o*-thiophan-5-one,



obtained from methylsuccinic acid and thiobenzylic acid, crystallises in truncated, double pyramids or microscopic, colourless, four-sided plates, softening at 156°, m. p. 160.5–162°. Towards concentrated sulphuric acid it behaves like the preceding compound. Its *silver* and *barium* salts form amorphous, white precipitates and rapidly decompose.

4:4-Diphenyl-2-methyl-2-carbethoxyethyl-1:3-oxathiophan-5-one,

$\text{CPh}_2\text{S}$   
 $\text{CO}-\text{O}-\text{CMe}-\text{CH}_2-\text{CO}_2\text{Et}$ , formed from ethyl acetoacetate and thiobenzylic acid, crystallises in drusy aggregates of colourless, four-sided prisms, m. p. 65–66.5°, and dissolves in alkali hydroxide solution and, with an orange coloration, in concentrated sulphuric acid.

*Ethyl carboxyphenylacetic acid*,  $\text{OEt}\cdot\text{CS}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ , obtained as sodium salt by the interaction of chlorodiphenylacetic acid and

potassium xanthate in presence of sodium carbonate, forms bundles of shining, colourless prisms, sintering slightly at  $140^{\circ}$ , m. p. about  $167^{\circ}$ . Its solution in concentrated sulphuric acid is bright red with a violet tinge, and becomes turbid and orange-brown when heated. The barium salt was prepared and analysed. Unsuccessful attempts were made to decompose the acid with formation of thiobenzyllic acid.

Improved yields of thiobenzyllic acid may be obtained by a modification of Becker and Bistrzycki's method (A., 1915, i, 245). The product given by Bettschart and Bistrzycki's method, which involves the use of the additive compound of benzyllic acid and allylthiocarbimide (A., 1919, i, 207), is less pure than that obtained with the help of phenylthiocarbimide.

Coupling of thiobenzyllic acid with acetophenone, benzophenone, dibenzyl ketone and benzil could not be effected. T. H. P.

**Syntheses in the Cinchona Series. IV. Nitro- and Amino-derivatives of the Dihydro-alkaloids.** WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1920, **42**, 1481—1489).—Using the methods described (compare D.R.-P. 283537), it was found that satisfactory results were not obtained in the preparation of 5-nitro- and 5-amino-dihydroquinine. During the nitration of dihydroquinine, sulphonation also occurred, and a nitrosulphonic acid was obtained. By nitration in fuming nitric acid (D. 1.52), however, without the addition of sulphuric acid, an excellent yield of 5-nitrodihydroquinine, m. p.  $220$ — $222^{\circ}$ ,  $[\alpha]_D^{25} - 200.0^{\circ}$  (in chloroform), was obtained. 5-Nitrodihydroquininesulphonic acid, m. p.  $260$ — $285^{\circ}$  (decomp.),  $[\alpha]_D^{25} - 133.0^{\circ}$  (in  $1/2$ -sodium hydroxide), was obtained either by nitration of dihydroquininesulphonic acid or by sulphonation of 5-nitrodihydroquinine.

5-Nitrodihydroquinine is best reduced by adding it slowly, with stirring, to cold, concentrated hydrochloric acid until it is all dissolved, and then adding stannous chloride to the solution at  $0^{\circ}$ , the temperature not being allowed to rise above  $35^{\circ}$ . The base was finally obtained in yellow needles, m. p.  $220$ — $221^{\circ}$ ,  $[\alpha]_D^{25} - 17.7^{\circ}$ .

These methods were successfully used for the preparation of nitro- and amino-derivatives from other dihydro-alkaloids of this series, the following compounds being obtained.

5-Nitroethylidihydrocupreine (5-nitro-optochin), m. p.  $225$ — $226^{\circ}$  (decomp.),  $[\alpha]_D^{25} - 198.2^{\circ}$  (in chloroform); 5-aminoethylidihydrocupreine, m. p.  $214$ — $215^{\circ}$  (decomp.),  $[\alpha]_D^{25} - 15.9^{\circ}$  (in alcohol) (compare Giemsa and Halberkann, A., 1919, i, 342).

5-Nitrodihydroquinidine, m. p.  $208$ — $209^{\circ}$ ,  $[\alpha]_D^{25} + 326.5^{\circ}$  (in alcohol), which gives a nitrate,  $C_{20}H_{21}O_4N_3HNO_3$ ,  $[\alpha]_D^{25} + 232.8^{\circ}$ ; 5-aminoethylidihydroquinidine, m. p.  $235^{\circ}$ ,  $[\alpha]_D^{25} + 115.5^{\circ}$  (in alcohol).

5-Nitroethylidihydrocupreidine, m. p.  $220$ — $221^{\circ}$  (decomp.),  $[\alpha]_D^{25} + 322.4^{\circ}$  (in alcohol); 5-aminoethylidihydrocupreidine, m. p.  $216$ — $217^{\circ}$ ,  $[\alpha]_D^{25} - 69.4^{\circ}$  (in chloroform),  $+ 91.6^{\circ}$  (in alcohol).

5-Nitrodihydrodeoxyquinine,  $C_{20}H_{21}O_9N_3 \cdot 3\frac{1}{2}H_2O$ , m. p. 67.5—69°,  $[\alpha]_D^{25} + 80.2^\circ$  (in alcohol). Attempts to reduce this compound were not successful.

W. G.

**Syntheses in the Cinchona Series. V. Dihydrodeoxyquinine and Dihydrodeoxyquinidine and their Derivatives.** MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1920, **42**, 1489—1502. Compare preceding abstract).—The series of compounds studied consisted of dihydroquinine  $\rightarrow$  chlorodihydroquinine  $\rightarrow$  dihydrodeoxyquinine  $\rightarrow$  dihydrodeoxycupreine  $\rightarrow$  ethyldihydrocupreine, and the similar series of quinidine derivatives, the methods of preparation employed being essentially those used by Koenigs (compare *Ber.*, 1895, **28**, 3147; 1896, **29**, 372) and Rabe (compare *A.*, 1910, i, 417) for the non-hydrogenated derivatives.

Dihydroquinine dihydrochloride when acted on by phosphorus pentachloride gives chlorodihydroquinine, m. p. 143—144°,  $[\alpha]_D^{25} + 42.1^\circ$  (in alcohol), giving a hydrochloride, m. p. 232—233° (decomp.),  $[\alpha]_D^{25} - 2.9^\circ$ , and on reduction dihydrodeoxyquinine,  $C_{20}H_{21}O_9N_3$ , an oil, which yields a crystalline trihydrate,  $[\alpha]_D^{25} - 77.5^\circ$  (in alcohol), a picrate, a hydrochloride, m. p. 179—180°,  $[\alpha]_D^{25} - 6.8^\circ$ , a dihydrochloride, and a methiodide,  $[\alpha]_D^{25} - 7.4^\circ$  (in alcohol). When demethylated by boiling with hydrobromic acid, dihydroquinine trihydrate yields dihydrodeoxycupreine, m. p. 191—191.5°,  $[\alpha]_D^{25} - 77.1^\circ$  (in alcohol), giving a hydrochloride, m. p. 210°,  $[\alpha]_D^{25} + 1.5^\circ$ , a dihydrobromide, m. p. 225—227°, a methiodide, m. p. 165—167°,  $[\alpha]_D^{25} - 37.6^\circ$  and ethyldihydrodeoxycupreine hydrochloride, m. p. 185—186°,  $[\alpha]_D^{25} - 9.0^\circ$ . When chlorodihydroquinine is demethylated by hydrobromic acid it yields bromodihydrocupreine dihydrobromide, m. p. 196—197°,  $[\alpha]_D^{25} - 69.1^\circ$ .

Chlorodihydroquinidine, m. p. 93.5—95°,  $[\alpha]_D^{25} + 20.0^\circ$  (in alcohol), gives a hydrochloride, m. p. 208—209°,  $[\alpha]_D^{25} + 39.7^\circ$ , and on reduction yields dihydrodeoxyquinidine dihydrate, m. p. 81—83°,  $[\alpha]_D^{25} + 167.8^\circ$  (in alcohol), giving a picrate, a hydrobromide, m. p. 151—152°,  $[\alpha]_D^{25} + 64.5^\circ$ ; a dihydrobromide, m. p. 225°, and a methiodide, m. p. 163—164°. When demethylated, dihydrodeoxyquinidine yields dihydrocupredine, m. p. 183—183.5°,  $[\alpha]_D^{25} + 183.7^\circ$ , giving a hydrochloride,  $[\alpha]_D^{25} + 76.8^\circ$ , a dihydrobromide, and a methiodide,  $[\alpha]_D^{25} + 95.0^\circ$ . Bromodihydrocupredine dihydrobromide has  $[\alpha]_D^{25} - 47.7^\circ$ .

Chloroquinidine gives a hydrochloride, m. p. 199—206° (decomp.),  $[\alpha]_D^{25} + 47.7^\circ$ ; deoxyquinidine gives a hydrochloride, m. p. 125°,  $[\alpha]_D^{25} + 81.9^\circ$ ; quinene gives a dihydrochloride, m. p. 110—115°,  $[\alpha]_D^{25} + 18.4^\circ$ .

The authors suggest that in place of the prefix "deoxy" (deoxy) the suffix "ane" should be used, e.g., in place of deoxyquinine they would use quinane.

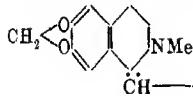
W. G.

**Constitution of Lycorine [= Narcissine].** K. GORTER (*Bull. Jard. bot. Buitenzorg*, 1920, [iii], 2, 1—7. Compare *A.*, this vol., i, 467).—Lycorine was obtained from the bulbs of *Crinum*

giganteum in a yield of 0.1-0.18% of the fresh material. Ewins' (narcissine) formula,  $C_{18}H_{21}O_4N$  (T., 1910, 97, 2406), was confirmed;  $[\alpha]_D^{25} - 120^\circ$ . The hydrochloride, m. p. 206°, is soluble in twenty parts of water at 26°. The mercurichloride, the picrate, and the perchlorate decompose, respectively, at 149°, 196°, and 230°. Asahina and Sugii (A., 1913, i, 1093) found that lycorine when heated with phloroglucinol and sulphuric acid gives a reddish-brown precipitate, indicating the presence of a methylenedioxy-group, already surmised by Ewins. Gorter has applied this reaction quantitatively by heating lycorine on the water-bath with 30% sulphuric acid, with and without resorcinol; the difference between the weight of the two precipitates corresponds roughly with that calculated for formalresorcinol from one methylenedioxy-group.

The above facts, and the blue fluorescence produced on adding a few drops of permanganate to lycorine sulphate solution, suggested a relationship to hydrastine, further emphasised by the opposite sign of the specific rotations of the free base ( $-120^\circ$ ) and of the hydrochloride ( $+43^\circ$ ).

With hydrogen and palladous chloride, lycorine is reduced to dihydrolycorine,  $C_{16}H_{20}O_4N$ , prisms, m. p. 247°, yielding a sparingly soluble nitrate, m. p. 243°. The reduced base is not made fluorescent by permanganate, whence the author concludes that the



hydroxyl of the supposed lactic acid side-chain is not adjacent to the *isoquinoline* nucleus, as in hydrastine, but rather that the fluorescence of lycorine is due to a double linking adjacent to this nucleus. Oxidation of lycorine with permanganate gave a small quantity of hydrastic and of oxalic acids, but no succinic acid, which leads the author to choose the annexed among various possible formulae.

G. B.

Ortho-para-isomerism in the Preparation of Diaminodiphenylmethane. HAROLD KING (T., 1920, 117, 988-992).

**Manufacture of Asymmetric Carbamides.** AXEL VIGGO BLOM (Brit. Pat. 125584).—Asymmetric carbamides are produced by the action of the calculated quantity of carbonyl chloride on equimolecular proportions of an aminouaphtholsulphonic acid and a primary aromatic dianiline in which the two aminogroups have different reaction speeds, in consequence of the presence of an ortho-substituent, as in the tolylenediamines, or of the substitution of one hydrogen atom by a formyl group. The operation must be conducted in such a way that the components are continuously brought into reaction in molecular proportions in a large vat, with efficient stirring, at a temperature of about 40° while a solution of an alkali hydroxide is run in in sufficient quantity just to neutralise the hydrogen chloride liberated. G. F. M.

**Preparation of Derivatives of *p*-Nitrophenylcarbamide.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 319970, from *Chem. Zentr.*, 1920, iv, 132-133).—*p*-Nitrophenylcarbamide chloride is caused to react with primary or secondary bases or their substitution products, particularly sulphonic acids, hydroxylsulphonic acid, etc., with or without reagents which absorb hydrogen chloride. The greenish-yellow lake-dye, *pp'*-dinitrophenylcarbamide, is obtained by heating *p*-nitrophenylcarbamide chloride with *p*-nitroaniline and nitrobenzene, or by the direct action of carbonyl chloride (1 mol.) on *p*-nitroaniline (2 mols.) if the initial temperature is not too high. Sodium sulphanilate and *p*-nitrophenylcarbamide chloride react in the presence of water and sodium acetate to yield sodium *pp'*-nitrophenylcarbamide-sulphonate, yellow, crystalline powder, sparingly soluble in water, which is reduced by sodium sulphide solution to the corresponding colourless, more readily soluble amino-compound. The dark yellow sodium *ethylenbis**pp'*-nitrodiphenylcarbamidesulphonate is prepared from sodium *pp'*-diaminostilbenesulphonate. H. W.

**Degradation Experiments with Dibromomaleic and Chlorofumaric Acids.** PAUL RUGGII and CARL HARTMANN (*Helv. Chim. Acta*, 1920, 3, 493-514).—The authors have subjected dibromomaleic acid to those reactions which, as a rule, convert an acid into an amine with one carbon atom less than the acid, the object being to obtain the brominated amine,  $\text{NH}_2\text{CBr}=\text{CBr}\text{NH}_2$ .

Ethyl dibromomaleate (compare Michael, A., 1893, i, 144; Punn, A., 1888, 1038; Ruhemann and Cunningham, T., 1899, 75, 902) may be prepared by heating an alcoholic solution of dibromomaleic anhydride and hydrogen chloride under pressure. Attempts to obtain tertiary glycols, and hence, by loss of water, dihydrofuran derivatives, by treating ethyl dibromomaleate with organomagnesium compounds, yielded unsatisfactory results. Ethyl hydrogen dibromomaleate,  $\text{CO}_2\text{H-CBr}=\text{CBr-CO}_2\text{Et}$ , crystallises in pale yellow, radiating needles, m. p. 65°-67°; Salmony and Simoni gave m. p. 100°, which is erroneous (A., 1905, i, 631).

*Dibromomaleic diamide*,  $\text{NH}_2\text{CO-CBr}=\text{CBr-CO-NH}_2$ , forms slender, colourless needles, turns brown at 120°, and decomposes with evolution of bromine at 200°. Treatment of the diamide with bromine in a sealed tube at 90° yields dibromomaleimide, m. p. 227° (compare Dunlap, A., 1896, i, 471).

The *hydrazine* salt of *dibromomaleichydrazide acid*,

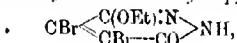


forms slender, white needles, m. p. about 130° (decomp.), and in the aqueous solution reacts with ammoniacal silver solution in the cold, whilst with neutral silver nitrate, silver dibromomaleate is precipitated. By dilute sulphuric acid, hydrazine sulphate is precipitated, and the action of benzaldehyde precipitates both the hydrazine molecules as benzylideneazine. By prolonged boiling

with dibromomaleic anhydride in alcoholic solution, the salt is converted quantitatively into the ammonium salt of

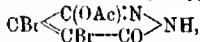
*Dibromomaleic hydrazide* [4:5-dibromo-3:6-diketo-1:2:3:6-tetrahydropyridazine],  $\text{CBr} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CBr} \end{smallmatrix} \text{CO} \begin{smallmatrix} > \\ \text{NH} \end{smallmatrix}$ , which forms yellow needles and is a highly stable compound; when slowly heated to above  $300^\circ$ , it gradually turns brown and decomposes, and when immersed in a bath at  $340^\circ$  it melts and decomposes. The ammonium salt,  $\text{C}_4\text{H}_2\text{O}_2\text{N}_2\text{Br}_2 \cdot \text{NH}_3$ , forms almost colourless crystals, and does not reduce ammoniacal silver solution. The two silver salts,  $\text{C}_4\text{HO}_2\text{N}_2\text{Br}_2\text{Ag}$  and  $\text{C}_4\text{O}_2\text{N}_2\text{Br}_2\text{Ag}_2$ , the barium salt ( $+ 6\text{H}_2\text{O}$ ), and other salts have been prepared.

4:5-Dibromo-3-ethoxy-6-keto-1:6-dihydropyridazine,



obtained by heating the di-silver salt of the preceding compound with ethyl iodide and alcohol, crystallises in white leaflets. m. p.  $206^\circ$ ; its silver salt was prepared, but not in a pure state.

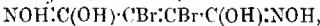
4:5-Dibromo-3-acetoxy-6-keto-1:6-dihydropyridazine.



forms crystals, sintering at  $223^\circ$ , m. p.  $228^\circ$ , and has the normal molecular weight in boiling alcohol.

*Ethylenediamine dibromomaleate*,  $\text{C}_4\text{H}_2\text{O}_4\text{Br}_2\text{C}_2\text{H}_8\text{N}_2$ , forms slender, white needles, turning brown at about  $170^\circ$ , and then decomposing.

*Dibromomaleic dihydroxamic acid*.



forms a hygroscopic, non-crystallisable mass; the sodium salt,  $\text{C}_4\text{H}_2\text{O}_4\text{N}_2\text{Br}_2\text{Na}_2$ , is also hygroscopic.

Chlorofumaric chloride,  $\text{COCl} \cdot \text{CCl} \cdot \text{CH} \cdot \text{COCl}$ , prepared from tartaric acid and phosphorus pentachloride (compare Perkin, T., 1888, 53, 696), may be freed from chlorides of phosphorus by shaking with water, if care be taken that no heating occurs. The diethyl ester of chlorofumaric acid, prepared by dropping alcohol on to the crude chloride (compare Claus, A., 1878, 855), gives vapour which strongly attacks the eyes.

*Ethyl pyrazolone-3-carboxylate*,  $\text{CO} \cdot \text{CH}_2 \begin{smallmatrix} > \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$  (compare

Rothenburg, A., 1893, i, 180, 367, 730; Ruhemann, T., 1896, 69, 1394), prepared by the interaction of ethyl chlorofumarate and hydrazine hydrate, forms crystals, m. p.  $178^\circ$ , and with fuming nitric acid yields a violet solution giving, on neutralisation, a violet compound, m. p.  $164^\circ$ .

*Bismonochlorofumarylhydrazine*,  $(\text{CO}_2\text{H} \cdot \text{CH} \cdot \text{CCl} \cdot \text{CO} \cdot \text{NH} \cdot)_2$ , obtained as hydrazine salt by the interaction of chlorofumaric chloride and hydrazine hydrate, forms almost colourless crystals, m. p. above  $360^\circ$ , and reduces ammoniacal silver solution in the

hot, but not Fehling's solution; it dissolves only in alkali solutions, giving deep yellow colorations. The *hydrazine salt*,

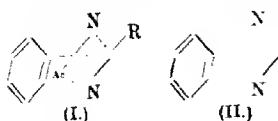


forms somewhat unstable, deep yellow crystals, m. p. 218°, and reduces Fehling's solution and ammoniacal silver solution immediately. T. H. P.

T. H. P.

**Structure- and Stereo-isomerism of Indazole Derivatives and the Constitution of Indazole.** KARL VON AUWERS and MARIANNE DÜESBERG (Ber., 1920, 53, [B], 1179-1210).—Further details of the preparation and properties of the 1- and 2-alkyl-indazoles are recorded (compare A., 1919, i, 455), and the corresponding quaternary salts have been fully investigated. It is shown that the 2-alkyl derivatives, like the 1-alkyl compounds, have the power of uniting with one molecular proportion of alkali iodide, but that a second proportion cannot be added, although the quaternary iodide still contains a tertiary nitrogen atom. Identical products are obtained by the action of the isomeric 1- and 2-alkyl-indazoles on the iodide of the same alkyl, but isomeric quaternary compounds result from the interaction of alkylindazoles with the iodide of a different alkyl radicle. Homologous alkylindazoles of the same series give different additive products with reciprocal homologous alkyl iodides, whilst homologous alkylindazoles of different series give identical results when similarly treated. The quaternary iodides liberate alkyl iodide when heated above their melting points. The 1-alkyl derivatives eliminate the added alkyl iodide, and thus re-form the parent substance; on the other hand, the 2-alkyl compounds lose the alkyl group of the base in the form of alkyl iodide, and retain the radicle of the iodide used, or, in other words, the product of fission is a 1-alkyl derivative. The observations are most readily explained by assuming the general structure  $\text{C}_6\text{H}_5\text{CH}_2\text{N}^{\text{R}'}\text{R}^{\text{R}}\text{N}^{\text{R}''}\text{R}^{\text{R}''}$ , for the quaternary iodides. A method of converting 2-alkylindazoles into 1-derivatives is thus given, and also the simplest and best method of preparing the latter in the pure state.

Further instances of stereoisomerism among acylindazoles are recorded, and more definite evidence is adduced that the observed phenomena are actually due to stereoisomerism. The capability to



yield such stereoisomerides disappears when an alkyl group is introduced into the 3-position. Apparently the possibility of stereoisomerism depends on the presence of a tervalent nitrogen atom in the ring, as

indicated by the annexed formulae, and the phenomena are thus similar to those recently observed by Freund and Kessler and by Hess. The apparent disappearance of stereoisomerism in the cases of the alkyl derivatives finds its parallel in the frequent formation

of stereoisomeric aldoximes and the infrequent occurrence of isomerides of the type of acetophenoneoxime.

The authors have attempted to bring all available chemical and physical evidence to bear on the problem of the elucidation of the constitution of indazole itself. They are led to the conclusion that this cannot at present be conclusively settled, but that the balance of the evidence is greatly in favour of formula I rather than II.



2-Methylindazole, prisms or plates, m. p. 56°, b. p. 261°/ordinary pressure, 135°/16 mm., is prepared from methyl iodide and indazole, from silver indazole and methyl iodide, and from 2-methylindazole-3-carboxylic acid at 230°; when crystallised from water, it appears to form a monohydrate (compare Schad, A., 1893, i, 280). It forms crystalline double *compounds* with silver nitrate and mercuric chloride. The *picrate* forms yellow, silky needles, m. p. 168°. 1-Methylindazole, m. p. 60—61°, b. p. 231°/ordinary pressure, 109°/17 mm., is prepared from 1-methylindazole-3-carboxylic acid, or by the alkylation of indazole with methyl iodide and sodium methoxide; the mixture of the 1- and 2-methyl derivatives obtained by the latter method is separable by fractional distillation under ordinary or diminished pressure, or by crystallisation of the picrates. 1-Methylindazole *picrate* forms slender, yellow needles or coarse, transparent crystals, m. p. 136—137°. 1-Methylindazole yields crystalline double *compounds* with mercuric chloride and silver nitrate. 1:2-Dimethylindazolium *iodide*, m. p. 187°, is prepared by heating either 1- or 2-methylindazole with an excess of methyl iodide at 100°; the corresponding *picrate* has m. p. 167—168°. 2-Ethylindazole is a pale yellow oil, b. p. 268°/ordinary pressure, 140°/14 mm.; the *picrate*, m. p. 155—156°, is immediately precipitated from dilute ethereal solution in the form of slender needles, which are gradually transformed into coarse, transparent crystals. 1-Ethylindazole is a colourless oil, b. p. 126—127°/21 mm. (*picrate*, thin, pale yellow needles, m. p. 148—150°). The action of ethyl iodide on 1-methylindazole or of methyl iodide on 2-ethylindazole at 100° leads to the production of 1-methyl-2-ethylindazolium *iodide*, small, colourless needles, m. p. 172.5—173° (*picrate*, m. p. 196—197°). 2-Methyl-1-ethylindazolium *iodide*, m. p. 154°, is similarly prepared from 2-methylindazole and ethyl iodide or 1-ethylindazole and methyl iodide; the corresponding *picrate* has m. p. 149—150°. 1:2-Diethylindazolium *iodide* forms coarse, colourless crystals, m. p. 134° (*picrate*, m. p. 153°). 2:3-Dimethylindazole, m. p. 79—80°, yields a *picrate*, m. p. 224—225°, and is converted by methyl iodide into 1:2:3-trimethylindazolium *iodide*, colourless, silky needles, m. p. 220—221°. Decomposition by heat proceeds normally in the cases of 1:2-dimethylindazolium iodide, 2-methyl-1-ethylindazolium iodide, and 1:2:3-trimethylindazolium iodide,

the product in the latter case being the 1:3-dimethyl derivative. 1-Methyl-2-ethylindazolium iodide yielded a mixture of 1-methyl-indazol (at least 75%) and 2-ethylindazole.

The stable form of 2-acetylindazole yields a crystalline *hydrochloride*, which is decomposed by exposure to moist air. The labile variety is completely transformed into the stable isomeride when heated for thirty minutes at 100°. The additive compound of the labile form and mercuric chloride has m. p. 174—175°. Hydrogen chloride decomposes the labile variety, with formation of indazole hydrochloride. Stable 2-propionylindazole, from indazole and propionic anhydride at the ordinary temperature, has b. p. 267°, m. p. 52°; it appears to be dimorphous. The labile *propionate* (from the silver salt or by the pyridine method) forms pearly leaflets or shining, rhombic plates, m. p. 100.5—101.5°; it has b. p. 267°, and is then quantitatively converted into the stable variety. The stable *benzoate* crystallises in slender, colourless needles, m. p. 94—95°. The labile *isomeride* forms small, coarse, colourless crystals, m. p. 78°; it can be distilled without decomposition at the ordinary pressure, and is thereby converted into the stable variety; the same change occurs slowly at the ordinary temperature, rapidly at 100°. Attempts to acetylate 3-methyl-indazole by methods similar to those outlined above in connexion with the propionyl derivative led only to the formation of 2-acetyl-3-methylindazole, m. p. 72—73°. Similarly, only one form of 2-acetyl-3-ethylindazole, slender prisms or large, well-defined crystals, m. p. 35.5—36.5°, could be prepared from 3-ethyl-indazole.

*o*-Nitrobenzoyl chloride is conveniently prepared by the action of thionyl chloride on *o*-nitrobenzoic acid, and is converted by ethyl methylacetooacetate and sodium into *ethyl o-nitrobenzoylmethylacetooacetate*, which is hydrolysed by sulphuric acid (1:1) to *o-nitropropiophenone*, pale yellow, viscous, odourless oil, b. p. 166—167°/15 mm., 161°/40 mm. (*semicarbazone*, m. p. 182—183°); it is reduced by a large excess of stannous chloride to *o-aminopropiophenone*, pale yellow leaflets or hexagonal platelets, m. p. 46—47° (*oxime*, needles, m. p. 88—89°). The aminoketone is converted according to the method of Fischer and Tafel into 3-ethylindazole, slender, interwoven needles or coarse prisms, m. p. 74.5—75.5°, b. p. 290° atmospheric pressure, 157—158°/15 mm. The *picrate* has m. p. 152.5—153.5°. 2:3-Diethyl-indazole, from 3-ethylindazole and ethyl iodide at 200°, is a colourless oil, b. p. about 287—290°, which does not show any tendency to crystallise; the *picrate* forms pale yellow needles, m. p. 184—186° after previous softening. H. W.

**Stereoisomeric Acyl Derivatives of Substituted Indazoles.**  
K. von AWERS and K. SCHWEGLER (*Ber.*, 1920, **53**, [B], 1211—1232). It has been shown previously (preceding abstract) that 2-acyl derivatives of indazole exist in two stereoisomeric forms of differing stability, whilst similar instances of stereo-

isomerism have not up to the present been observed with derivatives of the 3-alkylindazoles. The present communication deals with the effect of the entrance of substituents in the benzene nucleus. In every case which has been investigated, it has been found possible to isolate stereoisomeric acyl derivatives. The stability of the labile isomerides varies very greatly; in some instances the substances cannot be preserved unchanged for more than a few minutes, even at the ordinary temperature, whilst in others they can be heated for hours on the water-bath, and even maintained in the molten condition for a short time without undergoing transformation. The benzoyl derivatives are more stable than the corresponding acetyl compounds. In general, for some unexplained reason, the chemical nature of the substituent appears to have less influence on the stability of the derivative than has its position in the benzene nucleus. At present it is not possible to establish any definite connexion between the melting points and relative stabilities of the isomerides.

The stable acetyl and benzoyl derivatives are prepared by the action of warm acetic or benzoic anhydride on the indazoles. The labile compounds are obtained by the action of the requisite acid chloride on a suspension of the silver salt of the indazole in absolute ether; a few labile acetyl derivatives were prepared by the pyridine method. The following individual substances are described: 6-nitroindazole, m. p. 181° (2-acetyl derivative, stable form, m. p. 140—141°, labile form, colourless leaflets, m. p. 74—75°; 2-benzoyl derivative, stable form, m. p. 164—165°, labile form, yellowish-white, silky needles, m. p. 133—134° or 140° for different preparations). 6-Nitroindazole does not behave as definitely as indazole itself and its methyl derivatives towards methylating agents under varying conditions; thus, when heated with an excess of methyl iodide at 100°, it gives mainly 6-nitro-2-methylindazole, m. p. 159—160°, mixed, however, with 6-nitro-1-methylindazole, yellow, matted needles, m. p. 108—109°. When alkylation is effected in the presence of sodium methoxide, a mixture of the 1- and 2-methyl derivatives is likewise produced, the former being in excess. The constitution of 6-nitro-2-methylindazole is deduced by its reduction to 6-amino-2-methylindazole, long, intertwined needles, m. p. 156—157°, which, after diazotisation and elimination of the diazo complex, yields 2-methylindazole. 5-Nitroindazole, m. p. 208°, gives a stable acetyl derivative, m. p. 158—159°, and a labile compound, long, slender, silky needles, m. p. 138—139°; the corresponding stable benzoyl derivative crystallises in pearly leaflets, m. p. 193—194°, whilst the labile substance forms prisms, m. p. 155°, when plunged into a bath pre-heated to 150°, but otherwise depending on the rate of heating. 4-Nitroindazole, m. p. 202—203°, is converted into stable and labile acetyl derivatives, colourless, silky needles, m. p. 144.5—145.5°, and small, pale yellow needles, m. p. 119—121°, respectively; the stable benzoyl compound has m. p. 162—163°, whilst the labile form, pale yellow, slender needles, has m. p. 130—132°. 4-Nitroindazole is reduced

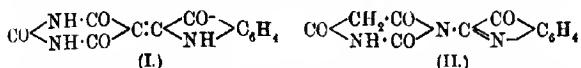
by ferrous sulphate and excess of ammonia to 4-aminoindazole, colourless, shining leaflets, m. p. 150—151.5° (the hydrochloride, nitrate, sulphate, and picrate, greenish-yellow needles, which decompose without melting at 175—180° after darkening at 170°, are also described). 2-Acetyl-4-acetylaminoindazole is prepared in a stable modification, colourless, shining leaflets, m. p. 201—202.5°, and a labile form, pale yellow crystals, m. p. 155—160°. When either variety is warmed with dilute hydrochloric acid, 4-acetylaminoindazole hydrochloride is obtained in long needles, m. p. 223—225°, from which the free base, coarse prisms, m. p. 145—148°, is isolated in the usual manner. 4-Cyanoindazole forms yellow, flat needles, m. p. 157—160°. 7-Nitroindazole, m. p. 186.5—187.5°, yields a very readily hydrolysed, stable acetate, m. p. 132.5—134°; the corresponding labile variety could not be isolated with certainty, apparently owing to its extraordinary ease of hydrolysis.

5-Chloro-*o*-toluidine, b. p. 118—120°/18 mm., is converted into its *benzoyl* derivative, colourless needles, m. p. 165—166°, which is transformed through the *nitroso*-derivative into 5-chloroindazole, slender, shining needles, m. p. 119—120° (picrate, m. p. 193—195°); its stable and labile *acetates* have m. p.'s 144—145° and 119—120° respectively.

5-Methylindazole, m. p. 117°, is conveniently obtained from benz-*o*-4-xylidide, which is converted into its unstable *nitroso*-compound, m. p. about 71—74°, which, when preserved in benzene solution, passes into the desired compound (picrate, thin, pale yellow needles or darker yellow needles grouped in rosettes, m. p. 169—170°). The stable *acetate* forms shining leaflets or flat needles, m. p. 49°, whilst the *labile* variety crystallises in colourless, transparent leaflets, m. p. 110—111°. The stable and labile *propionyl* compounds have m. p.'s 59—60° and 97—98° respectively, whilst the m. p.'s of the corresponding *benzoyl* derivatives are 89.5—90.5° and 120—121°. Treatment of 5-methylindazole with an excess of methyl iodide at 100° yields 2:5-dimethylindazole, coarse prisms, m. p. 76—77°, b. p. 270°/atmospheric pressure (the picrate, yellow, silky needles, m. p. 197—198°, mercuric chloride double salt, small, colourless prisms, m. p. about 220°, and silver nitrate additive compound, small, slender needles, m. p. 124.5—125.5°, are described). Alkylation with methyl iodide and sodium methoxide, on the other hand, appears to lead almost exclusively to the production of 1:5-dimethylindazole, colourless needles, m. p. 62—63° (picrate, m. p. 159—160°, mercuric chloride and silver nitrate additive compounds, m. p.'s 172—173° and 157—158° respectively). 6-Methylindazole, shining leaflets, m. p. 177—178° (picrate, m. p. 163.5—164.5°), forms an oily, stable *acetyl* compound, b. p. 146—147°/16 mm., and a labile derivative, colourless, shining leaflets, m. p. 116—118°. H. W.

**A New Indigoid Dyestuff. 5-(Dioxy-2:4-pyrimidine)-2-indoleindigo [5(2')-Indoxylpyrimidine-2:4:6-trione].** J. MARTINET and O. DORNIER (*Compt. rend.*, 1920, 171, 184—187).

When some of the technical fusion of indoxyl is added to an acetic acid solution of alloxan heated on a water-bath, 5(2')-indoxylpyrimidine-2:4:6-trione is obtained in opaque, violet needles. It dyes wool and silk heliotrope, and even has a certain affinity for cotton. Its sulphonio derivative dyes wool and silk violet. To this compound the authors assign the constitution I, although this



constitution has already been assigned by Felix and Friedländer (compare A., 1910, i, 278) to a compound prepared by them from barbituric acid and isatin anilide. They contrast the properties of these two compounds, and consider that the constitution of the latter compound is better represented by formula II. W. G.

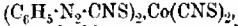
**Fission of Organic Dyes by Hydrogenation.** RICHARD MEYER (*Ber.*, 1920, **53**, [B], 1265—1276).—Alizarin direct violet R and alizarin direct green G of the Höchst Farbwerke are decomposed by hydriodic acid with the formation of leucoquinizarin and *p*-toluidine-2-sulphonic acid, and are thus isomeric with alizarin isrol and alizarin cyanine green G of the Farbeufabriken Friedr. Bayer & Co., which, when similarly treated, give leucoquinizarin and *p*-toluidine-3-sulphonic acid. It is remarkable that whilst *p*-toluidine-2-sulphonic acid condenses readily with quinizarin or leucoquinizarin, *p*-toluidine-3-sulphonic acid is unable to undergo such condensation, possibly because of internal salt formation between the neighbouring amino- and sulphonic groups.

The utility of concentrated hydriodic acid in effecting the fission of azo-dyes has been examined in a number of instances and its efficiency compared with that of sodium hyposulphite. In general, an aqueous or alcoholic solution of the dye is heated with an excess of concentrated hydriodic acid until action appears to be complete; the liberated iodine is removed by sulphurous acid and the hydriodic acid by evaporation with concentrated hydrochloric acid. The method has the great advantage over other reduction processes that it does not introduce any inorganic salts into the solution. Methyl-orange is decomposed by sodium hyposulphite or by hydriodic acid into *p*-aminodimethylaniline (acetyl derivative, m. p. 130°) and sulphamic acid, whilst diphenylamine-orange gives *p*-aminodiphenylamine, m. p. 66°, and sulphamic acid. Metanilic acid and *p*-aminodiphenylamine are obtained from metanil-yellow, whilst Congo-red yields benzidine and 1:2-naphthylenediamine-4-sulphonic acid. Naphthylene-red gives 1:5-naphthylenediamine and 1:2-naphthylenediamine-4-sulphonic acid. H. W.

New Catalytic Elements for the Transformation of Diazotised Compounds. A. KORCZYNSKI, W. MROZINSKI, and W. VIELAU (*Compt. rend.* 1920, 171, 182-184).—In certain of the changes brought about in the Sandmeyer reactions it is found

that the copper salt may quite well be replaced by the corresponding nickel or cobalt salt. Thus the double cyanide of nickel and potassium may replace that of copper and potassium for the preparation of nitriles from the corresponding diazonium salts. Cobalt is not satisfactory for this change.

Cobalt thiocyanate is an excellent catalyst for the conversion of diazonium salts into the corresponding thiocyanate, and in this case the intermediate double compound could be isolated from benzene-diazonium chloride. It had the constitution



and was obtained as a malachite-green, crystalline powder.

The preparation of chloro- or bromo-benzene from benzene-diazonium chloride or bromide by the nickel or cobalt haloids only resulted in very poor yields, and took place only in boiling solution.

Zinc and iron salts showed no sign of any catalytic action for these changes.

W. G.

**Preparation of Methyl Red.** LOUIS DESVRAGNES (*Ann. Chim. anal.*, 1920, [ii], 2, 209-210).—A solution of 89 grams of sodium nitrite in 150 c.c. of water is added slowly, with stirring, to a mixture of 137 grams of anthranilic acid, 1000 grams of water, 222 c.c. of hydrochloric acid (22°), and 300 grams of powdered ice. During the addition the temperature must not rise above 5°. After twenty minutes the mixture is added to 121 grams of dimethylaniline dissolved in 90 c.c. of hydrochloric acid (22°) and 200 c.c. of water, and, when the mixture has been stirred for a few minutes, 15 grams of sodium acetate dissolved in 500 c.c. of water are introduced. The purple-red crystals which form (in a few hours) are collected, washed with cold water, dried at 50°, and recrystallised from alcohol.

W. P. S.

**The Classification of the Proteins.** PIERRE THOMAS (*Bull. Soc. chim. Biol.*, 1920, 2, 112-118). The existing classifications are reviewed, and the desirability of adhering to a simple and uniform international scheme is emphasised.

J. C. D.

**Barger's Microscopical Method of Determining Molecular Weights. II. Its Application to Caseinogen.** KUMAO YAMAKAMI (*Biochim. J.*, 1920, 14, 522-533).—The author confirms the observation of Robertson ("The Physical Chemistry of Proteins," 1918) that the molecular and ionic concentration of alkali caseinogenate solutions of neutral and alkaline reaction is conditioned by the concentration of the alkali solution in which the caseinogen is dissolved. The osmotic concentration of alkali caseinogenate solutions of acid reaction is dependent on the amount of dissolved caseinogen, and the mean weight of the ions in solution is about 2000.

The solubility of caseinogen in alkali solutions containing a certain amount of alkali chloride is almost twice that of caseinogen in pure alkali solution. This probably offers an explanation of the high solubility figures obtained by Robertson (*loc. cit.*) and Van Slyke

and Bosworth (A., 1913, i, 660). The true solubility of caseinogen in pure alkali must be  $22.5 - 25 \times 10^{-5}$  gram-equivalent alkali per gram caseinogen, and the molecular weight of alkali caseinogenate which is soluble in distilled water must be 4000—4400. W. G.

**The Influence of Salts on the Optimum Condition of Precipitation of Caseinogen.** L. MICHAELIS and ALBERT v. SZENT-GYÖRGYI (*Biochem. Zeitsch.*, 1920, **103**, 178—185).—The change in the optimum condition of precipitation of caseinogen by acetic acid and sodium acetate in the presence of salts is brought about by the action of the anion and the cation of the salts. When the action of the cation is stronger, the optimum flocculation is shifted to the less acid zone and vice versa. When the activity of both ions is the same no change in the optimum takes place. A table and curves of the results obtained with various salts are given.

S. S. Z.

**The Mode of Action of Chlorine on Oxyhaemoglobin.** ANDRÉ MAAYER and FRED VILES (*Bull. Soc. chim. Biol.*, 1920, **2**, 96—111).—A series of products are formed, which are characterised by their spectra, during the action of chlorine on haemoglobin. It is probable that following the inhalation of large doses of chlorine the same series of reactions occurs as may be obtained *in vitro*.

J. C. D.

**Hæmocyanin. IV. Visible Absorption Spectrum of Oxyhæmocyanin.** C. DUFÉRE and A. BURDEL (*J. Physiol. Path. gen.*, 1920, **18**, 683—701).—The results of these spectrographic studies show that the oxyhæmocyanins of the gastropod molluscs of the cephalopods and of both the marine and fresh-water crustaceans give a clear and intense absorption band in the yellow when examined in suitable concentrations and solvents. The solutions examined were sufficiently clear and yet rich enough in pigment to give the characteristic band when intense illumination was employed. The solutions of oxyhæmocyanin do not contain tetroerythrin in appreciable quantities. Slight variations in the axis of absorption are considered as due to differences in the amounts of electrolytes present in the solutions examined. Photographs are appended.

Chemical Abstracts.

**Acidity of Ash-free and of Commercial Gelatin Solutions.** H. E. PATTER and T. O. KELLEMS (*J. Biol. Chem.*, 1920, **42**, 363—366).—The isoelectric point of ash-free gelatin lies at  $p_H = 4.8$ , corresponding with a hydrogen-ion concentration of  $1.59 \times 10^{-5}$ , and that of commercial gelatin at  $p_H = 5.64$ , with hydrogen-ion concentration  $2.28 \times 10^{-5}$ . The displacement of the isoelectric point of commercial gelatin is due to its alkali content. W. G.

**Effect of Salts of Heavy Metals on a Protein and the Reversal of such Effects.** ROBERT A. KENOE (*J. Lab. Clin. Med.*, 1920, **5**, 443—452).—The coagulation of gelatin, under the

influence of salts of heavy metals, is not an irreversible reaction, but may be reversed through the action of alkalis or the neutral salts of the alkali and alkaline-earth metals. Not all such salts are of the same value in producing this effect, there being a marked secondary dependence on the acid radicle combined with the metal. Thiocyanates and iodides are more effective than bromides and chlorides. Reversal occurs most readily if the alkali or salt is added soon after the coagulation of gelatin by the heavy metal has been caused, and if heat is used. Coagulation of gelatin by heavy metals may be completely inhibited by the previous or simultaneous addition of alkalis or salts of the alkali or alkaline earth metals in sufficiently high concentrations, even when these are not of such nature as to combine with the coagulant. It is suggested that the metals react with the gelatin to form definite compounds as do the same metals with the fatty acids to form soaps. On the basis that the poisonous effects of the heavy metals on the body are due to coagulation of body proteins, the author believes that the administration of alkalis and salts of the alkali and alkaline-earth metals would be of benefit in lead and mercury poisoning, by reversing the coagulation of the proteins.

## CHEMICAL ABSTRACTS.

**Relation between the Internal Complex Metallic Salts and the Solubility of Silk in Ammoniacal Nickel Solutions. The Biuret Reaction (Cu, Ni, Co) of Silk and Wool.** M. BATTEGAY and THÉONORE VOLTZ (*Bull. Soc. chim.*, 1920, [iv], 27, 536—540).—The colour changes and ultimate solution of silk when it is immersed in an ammoniacal solution of a nickel salt are explained as due to the formation of a complex nickel salt with a cyclic structure. The changes occurring are considered to be similar to those of the biuret reaction, and it is shown that under suitable conditions similar colour reactions may be obtained with silk and alkaline solutions of copper and cobalt salts.

When wool is dissolved in warm aqueous sodium hydroxide and to the solution an excess of copper sulphate is added, a rose-coloured liquid is obtained after filtration. Nickel salts give similar phenomena. Similar results are also obtained if the wool is first partly hydrolysed by acid and then treated with alkali and copper sulphate.

W. G.

**Does Chloropicrin Act on the Soluble Ferments?** GABRIEL BERTRAND and (MME) ROSENBLATT (*Compt. rend.*, 1920, 171, 137—139).—Chloropicrin was found to possess only a very slight inhibiting influence on the action of the various soluble ferments, sucrase, amygdalinase, urease, catalase, zymase, laccase, and tyrosinase, which were examined.

W. G.

**Silicon as a Substitute for Carbon in Organic Compounds.** ARTUR BYGNÉN (*Diss., Uppsala*, 1916, pp. 189).—A historical summary of the chemistry of silicon compounds and their relation to the corresponding carbon compounds is given, followed by a study of the physical relations between the two classes of substances.

Mono-derivatives,  $RSiCl_3$ , are easily obtained in most cases, disubstituted derivatives are very difficult to prepare, whilst tetrasubstituted derivatives are the most easily obtained because an excess of the Grignard reagent can be used.

The b. p.'s under diminished pressure and the densities at different temperatures of the following compounds are recorded:  $RSiCl_3$ , where  $R = Et, Pr, butyl, isobutyl, isoamyl, Ph$ , and  $CH_2Ph$ ;  $R_2SiCl_2$ , where  $R = Et$  and  $Pr$ ;  $RSiEtCl_2$ , where  $R = Pr, isobutyl$ , and  $Ph$ ;  $SiR_4$ , where  $R = Me$  and  $Et$ ;  $SiR_2R'$ , where  $R = Me$  or  $Et$  and  $R' = Et, Pr, butyl, isobutyl, isoamyl, Ph$ , and  $CH_2Ph$ ;  $SiMe_2R_2$ , where  $R = Et$  and  $Pr$ ;  $SiMeEtR_2$ , where  $R = Pr, isobutyl$ , and  $Ph$ ;  $CH_2\begin{matrix} < \\ -CH_2 \cdot CH_2 \\ > \end{matrix} SiR_2$ , where  $R = Cl$  and  $Me$ .

*Benzyltrimethylmethanesulphonic acid*, rectangular tablets with  $2H_2O$ , m. p. (anhydrous)  $142\cdot2-144\cdot2^\circ$ , obtained by shaking the hydrocarbon with fuming sulphuric acid (6%  $SO_3$ ), forms the salts ammonium, potassium ( $1H_2O$ ), sodium ( $2H_2O$ ), lithium ( $1H_2O$ ), calcium ( $0\cdot5H_2O$ ), strontium ( $2H_2O$ ), barium ( $3H_2O$ ), magnesium ( $7H_2O$ ), zinc ( $6H_2O$ ), cadmium ( $3H_2O$ ), ferrous ( $7H_2O$ ), nickel ( $8H_2O$ ), cobalt ( $8\frac{1}{2}H_2O$ ), lead ( $2H_2O$ ), copper ( $6H_2O$ ), and silver ( $1H_2O$ ). The acid chloride, tablets or prisms, m. p.  $58\cdot7-59\cdot2^\circ$ , acid bromide, m. p.  $65\cdot5-66^\circ$ , amide, needles or scales, m. p.  $101^\circ$ , methylamide, m. p.  $94\cdot8-95\cdot3^\circ$ , anilide, m. p.  $137^\circ$ , methylanilide, m. p.  $97\cdot8-98^\circ$ , o-toluidide, leaflets, m. p.  $156-157^\circ$ , p-toluidide, m. p.  $117-118\cdot2^\circ$ , and benzylamide, m. p.  $141\cdot5-141\cdot7^\circ$ , are described. By fusion with potassium hydroxide the potassium salt is converted into  $\beta\beta\beta$ -trimethylethylphenol,  $CMe_3CH_2C_6H_4OH$ , needles, m. p.  $118-118\cdot2^\circ$ .

CHEMICAL ABSTRACTS.

## Physiological Chemistry.

**Further Data Concerning the Alleged Relation of Catalase to Animal Oxidations.** RAYMOND L. STEHLE and ARTHUR C. McCARTY (*J. Biol. Chem.*, 1920, **42**, 269-272. Compare A., 1919, i, 561).—Measurements were made of the carbon dioxide production, and haemoglobin and catalase contents of rabbit and cat blood drawn to correspond as nearly as possible with successive periods of normal and high metabolism. Contrary to Burge's hypothesis (compare A., 1919, i, 233), these experiments demonstrate that there may be great variations in the rate of animal metabolism without any change in the catalase content of the blood. W. G.

**Manganese Content of Human Blood and Tissues.** CLARENCE K. REIMAN and ANNIE S. MINOT (*J. Biol. Chem.*, 1920, **42**, 329-345).—See this vol., ii, 558.

**Exchange of Chloride Ions and of Carbon Dioxide between Blood Corpuscles and Blood Plasma.** L. S. FRIDERICIA (*J. Biol. Chem.*, 1920, **42**, 245-257).—The author confirms the results of Van Slyke and Cullen (A., 1917, i, 521) as to the influence of the carbon-dioxide tension on the partition of the chlorides between plasma and red corpuscles, and shows that the cause of the exchange of chloride ions between plasma and corpuscles is in the red corpuscles and not in the plasma. The amount of chloride ions passing from the plasma into the corpuscles by increasing the carbon-dioxide tension from 0.08 to 162 mm. almost completely accounts for the increased carbon-dioxide combining power gained by the plasma. Increasing carbon-dioxide tension increases the carbon-dioxide combining power of both plasma and corpuscles, but the hydrogen-ion concentration remains almost the same in plasma and corpuscles at different carbon-dioxide tensions. Hasselbach's explanation of the properties of haemoglobin (A., 1917, i, 490) offers an interpretation of both of these phenomena.

W. G.

**Metabolism of Carbohydrates. I. Stereochemical Changes undergone by Equilibrated Solutions of Reducing Sugars in the Alimentary Canal and in the Peritoneal Cavity.** JAMES ARTHUR HEWITT and JOHN PRYDE (*Biochem. J.*, 1920, **14**, 895-405).—See this vol. i, 508.

**The Metabolism of Sulphur. III. The Relation between the Cystine Content of Proteins and their Efficiency in the Maintenance of Nitrogenous Equilibrium in Dogs.** HOWARD B. LEWIS (*J. Biol. Chem.*, 1920, **42**, 289-296).—A study of the relative efficiencies in nutrition of casein, a protein low in cystine content, and of serum albumin, high in cystine content, for dogs. Under conditions of low protein intake, serum albumin is more effective in maintaining nitrogenous equilibrium than is casein. When casein is supplemented by cystine, however, it is as efficient as serum albumin for the maintenance of nitrogenous equilibrium.

W. G.

**The Fat-soluble Growth-promoting Substance in Lard and Cotton-seed Oil.** AMY L. DANIELS and ROSEMARY LOUGHIN (*J. Biol. Chem.*, 1920, **42**, 359-362).—Both lard and cotton-seed oil apparently contain appreciable amounts of the fat-soluble growth-promoting substance, as is shown by the growth of rats on a diet containing either of these fats and otherwise devoid of the fat-soluble vitaminine.

W. G.

**Vitamine Studies. V. The Antiscorbutic Properties of Raw Beef.** R. ADAMS DUTCHER, EDITH M. PIERSON, and ALICE BIESTER (*J. Biol. Chem.*, 1920, **42**, 301-310).—Guinea-pigs were fed on a diet of oats, water, and an amount of autoclaved milk sufficient to improve the diet, but insufficient to prevent scurvy. The animals developed scurvy and died. The addition of water extracts of raw, lean beef equivalent to 5, 10, 15, or 20 grains of

beef had no effect on the time of onset of scurvy or on the length of life of the animals. That the beef extract contained no deleterious ingredient was shown by the fact that when orange juice was added to the diet in addition to the beef juice, there was no scurvy and the animals were in excellent condition.

W. G.

**Lipase of Pulmonary Tissue.** ANDRÉ MAYER and PIERRE MOREL (*Bull. Soc. chim. Biol.*, 1919, 1, 189--207).—Pulmonary tissue contains an enzyme which hydrolyses esters and glycerides, and has properties different from those of pancreatic lipase.

J. C. D.

**Action of Extracts of the Spleen on the Smooth Muscle Tissues. Preparation and Nature of the Active Principle.** L. STERN and E. ROTHLIN (*J. Physiol. Path. gen.*, 1920, 18, 753--780).—The authors attempt to isolate the active principle of extracts of the spleen, which produces hypertonic conditions in organs containing smooth muscle tissue. Fresh spleens were cleaned from fat and connective tissue and ground to a pulp. The macerated tissue was boiled for half an hour in 2 to 3 vols. of water made slightly acid with acetic acid, and filtered. The filtrate was then heated just to the b. p., and sodium chloride and acetic acid were added until no more precipitation occurred. After filtering, the filtrate (usually clear) was evaporated on a water-bath to one-tenth the original volume. The material separating out on cooling was removed by filtration or centrifuging, and the liquid evaporated to dryness, powdered, and kept in a desiccator over sulphuric acid or calcium chloride. The product is soluble in water and very active in producing hypertonicity; 25 to 30 grams of substance result from 1 kilo. of spleen. The ethereal extract of the powder when dried and dissolved in salt solution is ineffective in producing contraction of smooth muscle. An extract of the powder made with slightly acidified ethyl alcohol is, however, quite as active as an equivalent amount of the original preparation. During the evaporation of the ethyl-alcoholic extract, insoluble material settles out, which is removed by filtration or centrifugation, and the residual liquor evaporated to dryness. A dark brown, hygroscopic powder results. The further purification of the compound is best effected by precipitation with phosphotungstic acid, and gives a product some sixty times as effective. The preparation is named "*liénine*" by the authors, who consider from physiological experiments that its action is through a direct effect on the smooth muscle fibres, thus differentiating it from adrenaline, which acts by intermediation of the nerve elements. Liénine is thus similar in action to  $\beta$ -amino-4-ethylglyoxaline. In view of these results, particular interest is attached to the spleen. It appears as if this organ can be considered as exercising an action on the general economy in retarding the exchanges and counterbalancing the action of other organs.

for example, the thyroid, such splenic function being due, in part at least, to histamine, representing as it does a product of internal secretion or functional activity.

CHEMICAL ABSTRACTS.

**Evidence Indicating a Synthesis of Cholesterol by Infants.**  
 JAMES L. GAMBLE and KENNETH D. BLACKFAN (*J. Biol. Chem.*, 1920, **42**, 401-409).—For the estimation of cholesterol in milk and stools, the authors recommend a modification of the method of Autenreith and Funk (*Münch. med. Woch.*, 1913, **60**, 1243), the non-saponifiable material being separated from the soaps by using diluted alcohol and light petroleum (compare Kumagawa and Suto, *A.*, 1908, ii, 331).

Analyses of the non-saponifiable fraction of infants' stools confirm the observation of Müller (compare *A.*, 1900, ii, 289) that in the case of infants on a continued milk diet, cholesterol is excreted in the stools without undergoing change to any appreciable extent into coprosterol. From determinations of the cholesterol intake and excretion of four infants over a period of three days, during which the subjects were gaining in weight and receiving a usual amount of cholesterol, it is shown that the cholesterol excreted was 1.7 to 3.4 times that which was present in the food.

W. G.

**Decomposition of Propionic Acid in the Animal Body.**  
 LÉON BLUM and PIERRE WÖRINGER (*Bull. Soc. chim. Biol.*, 1920, **2**, 88-95).—Lactic and pyruvic acids were found in the urine following the administration of propionic acid to dogs and rabbits. These products probably arise in the body by oxidation of the  $\alpha$ -carbon atom of the injected acid. The authors compare this with the oxidation of the  $\alpha$ -carbon atom in the degradation of the  $\alpha$ -amino-acid molecule in the animal organism. The question whether lactic acid or pyruvic acid is the first to be formed is fully discussed, but an opinion is postponed until further researches have been completed.

J. C. D.

**The Influence of Chemical Constitution on the Toxicity of Organic Compounds to Wireworms.** F. TATTERSFIELD and A. W. R. ROBERTS (*J. Agric. Sci.*, 1920, **10**, 199-232).—The authors have examined a very large number of organic compounds with respect to their toxic action on wireworms, and from their results certain general conclusions may be drawn as to the relationship between chemical constitution and toxicity.

The general effect of a class of compounds of the same type is directly determined by the chemical constitution of the type, but the particular effects of individual members of a class are limited by their physical properties, such as volatility. On the whole, aromatic hydrocarbons and their halogen derivatives are more toxic than the aliphatic hydrocarbons and their halogen derivatives. The substituents which influence toxicity most when introduced singly into the benzene ring are, in decreasing order of effectiveness:

ness: methylamino-, dimethylamino-, hydroxy-, nitro-, amino-, iodine, bromine, chlorine, methyl groups. This order is, however, modified in the presence of a second substituent; thus, for example, when there is a methyl group already present in the ring, the order becomes: chlorine (in the side-chain), amino-, hydroxy-, chlorine (in the ring), methyl. When chlorine and hydroxy-groups are present together, they give rise to highly toxic substances, and the association of chlorine and nitro-groups in chloropicrin gives rise to one of the most toxic substances tested. Methyl groups introduced into the amino-group of aniline increase toxicity more than if substituted in the ring.

Compounds with irritating vapours, such as allylthiocarbimide, chloropicrin, benzyl chloride, usually have high toxic values, these values not being closely correlated with the vapour pressures or rates of evaporation of these substances.

There is a fairly close relationship between toxicity and vapour pressure, rate of evaporation, and volatility in the case of compounds of the same chemical type. Thus, in a series of similar compounds, decrease in vapour pressure and volatility is usually associated with an increase in toxicity. A limit is put on toxicity by the decrease in vapour pressure, which may sink too low to permit of a toxic concentration in the vapour phase. Chemically inert compounds boiling above 170° are usually uncertain in their toxic effect on wireworms, even after an exposure for 1000 minutes at 15°. Nearly all organic compounds boiling above 215° are uncertain in their action, whilst those boiling above 245° are non-toxic, although these limits depend to some extent on the resistance of the insect, the length of exposure, and the temperature at which the experiment is carried out.

W. G.

### Chemistry of Vegetable Physiology and Agriculture.

**Action of a Bulgarian Ferment on Maltose and Sucrose.**  
GEN ITSU KITA (*Bull. Soc. chim. Biol.*, 1920, 2, 140-142).—This enzyme has no action on maltose or sucrose, as has previously been stated by Bertrand and Ducháček (A., 1909, i, 623).

J. C. D.

**The Fermentation of Dextrose, Galactose, and Mannose by *Lactobacillus pentoaceticus*, n.sp.** W. H. PETERSON and E. B. FRED (*J. Biol. Chem.*, 1920, 42, 273-287).—[With J. A. ANDERSON.]—The aldoses, dextrose, galactose, and mannose are fermented by *Lactobacillus pentoaceticus*, n.sp., with the production of lactic acid, ethyl alcohol, carbon dioxide, and small amounts of acetic acid. Dextrose and galactose are fermented at approxim-

ately the same rate and to the same extent, but mannose is more slowly attacked and less sugar is consumed. The difference is probably explicable by the configuration of the sugars.

The acetic acid obtained during the fermentation is probably produced by secondary fermentation of the lactic acid formed.

W. G.

**The Nature of Yeast Fat.** IDA SMEDLEY MACLEAN and ETHEL MARY THOMAS (*Biochem. J.*, 1920, **14**, 483-493).—Palmitic, oleic, and linoleic acids have now been identified with certainty in yeast fat, but the pentadecenoic acid previously described (Hinsberg and Roos, A., 1903, ii, 565; 1904, ii, 760) is a mixture of palmitic and lauric acids. An acid, m. p. 77°, was isolated (compare Neville, A., 1913, i, 1026), and is possibly arachidic acid. The authors were unable to confirm the presence of the dodecenoic acid described by Hinsberg and Roos (*loc. cit.*).

The sterol, present to the extent of about 20% of the total yeast, being partly in the free state and partly as fatty acid esters, is apparently identical with Tanret's ergosterol (A., 1889, 407). It is probable that the mycosterol isolated from certain fungi by Ikeguchi (this vol., i, 160) is also identical with ergosterol, and that this sterol is characteristic of the whole group of cryptogams. Yeast sterol is differentiated from the sterols of the higher plants and animals by the presence of three double bonds in its molecule.

W. G.

**Water Culture Experiments with Different Nutrient Solutions; Influence of Manganese and Hydrogenion Concentration.** FR. WEIS (*K. Vet.-Landbohøjskole Aarskrift*, 1919, 239-280; from *Chem. Zentr.*, 1920, iii, 99).—Manganese sulphate added to culture solutions in an amount equivalent to their normal iron content does not exert a beneficial influence on the growth of plants. The most favourable hydrogen-ion concentration for the classes of plants investigated was  $p_H = 4.5-6.0$ .

H. W.

**Action of Chromium and Manganese on Plant Growth.** TH. PFEIFFER, W. SUMMERMACHER, and A. RIPPEL (*Fuhlings Landw. Zeit.*, 1918, **17** 18, 313; from *Bied. Zentr.*, 1920, **49**, 259-263).—Experiments on oats and barley treated with an ordinary fertiliser and with small proportions of chrome iron ore or potassium dichromate fail to reveal any beneficial effect of the chromium (compare König, A., 1911, ii, 524). Similar experiments on oats treated with manganese sulphate indicate that the effect of the manganese is at most very minute.

T. H. P.

**Are Vitamines Necessary for the Development of Plants?** AUGUSTE LUMIÈRE (*Compt. rend.*, 1920, **171**, 271-273).—The author finds that fresh brewer's yeast heated to 135°, and no longer capable of curing polyneuritis in pigeons, gives a bouillon which considerably improves the development of fungi grown on poor culture solutions. As a result of these and further experiments, the

author concludes that vitamins, as ordinarily characterised, are not essential for the development of plants. W. G.

**Chemical Components of Green Plants. II. Presence of a Mixture of Unsaturated Alcohols in many Green Plants.**

HARTWIG FRANZEN and ADOLF WAGNER (*Sitzungsber. Heidelberg Akad. Wiss. Math. nat. Klasse, Abt. A*, 1920, 2 reprints, pp. 4; from *Chem. Zentr.*, 1920, iii, 95).—The mixture of unsaturated alcohols found previously in the leaves of beech and chestnut is shown by its characteristic odour to be present also in the leaves of all classes of plants investigated (forty have been examined). The distillate from the mountain ash also contained hydrocyanic acid, whilst a component with an intense odour of lemons (citral) was present in that from strawberry leaves. The first distillate from certain plants (wormwood, dahlia, peppermint, ivy) contained notable amounts of essential oils. H. W.

**The Presence of Copper in Plants and Particularly in Foodstuffs of Vegetable Origin.** B. GUÉRITAULT (*Compt. rend.*, 1920, **171**, 196—198).—The author has determined the percentage of copper present in a large number of fruits, vegetables, and seeds, and finds that the amount varies from 0.0087 to 0.0636% of the ash, and from 1.1 to 17.1 mg. per kilo. of fresh material. W. G.

**The Odorous Constituents of Apples. Emanation of Acetaldehyde from the Ripe Fruit.** FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1920, **42**, 1509—1526).

The odorous constituents of apples were found to consist essentially of the amyl esters of formic, acetic, and hexoic acids, with a very small amount of the octoic ester. In addition, there was a considerable proportion of acetaldehyde and probably some free acid. The aqueous distillate from fresh apple parings also contained exceedingly small amounts of methyl and ethyl alcohols and furfuraldehyde, the latter probably arising from some chemical change during the distillation. The essential oil obtained from apple parings amounted to 0.0035% in the case of Ben Davis apples and 0.0043% in the case of crab apples.

Acetaldehyde is a product of the vital activities of the fruit, and occurs in the exhalations from ripe apples. W. G.

**The Extraction of the Fat-soluble Factor of Cabbage and Carrot by Solvents.** SYLVESTER SOLomon ZILVA (*Biochem. J.*, 1920, **14**, 494—501).—Alcohol extracts the fat-soluble factor from cabbage and carrots. An amount of such extract equivalent to 10—12 grams of fresh carrots given daily is sufficient to promote normal growth in rats subsisting on a diet lacking the fat-soluble factor. In addition, the alcoholic extract from carrots contains the antineuritic and, to a smaller extent, the antiscorbutic factors. An ethereal extract from the alcoholic fraction equivalent to 25 grams of fresh carrots promoted recovery and renewed growth in rats

which were declining in weight on account of a fat-soluble factor deficiency.

W. G.

**The Occurrence of Water-soluble Vitamine in some Common Fruits.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1920, **42**, 465—489).—[With ALFRED J. WAKEMAN.]—The fresh juices of the edible parts of the orange, lemon, and grapefruit contain water-soluble *B* vitamine, the potency of the juices in this respect being similar, for equal volumes, to that of cow's milk. These juices may be suitably desiccated on starch without losing their efficiency. Grape juice was less potent than the fruit juices mentioned above. The edible portions of apples and pears furnish some water-soluble *B*, but from a comparative standpoint they cannot be regarded as rich in this factor; prunes are apparently somewhat richer.

From preliminary experiments it is doubtful whether the juices of lemon or grapefruit contain more than traces, if any, of the fat-soluble vitamine, though orange-juice would appear to contain some of this vitamine.

W. G.

**Spilanthal, the Pungent Principle of Para Cress (*Spilanthes oleracea*).** I. YASUHIKO ASAHINA and Michizō ASANO (*J. Pharm. Soc. Japan*, 1920, No. 460, 503—515).—Gerber (A., 1903, ii, 609) isolated the pungent principle of Para cress, spilanthal,  $C_{15}H_{64}O_2N_2$ , as a syrup, which, when heated with alcoholic hydrochloric acid in a sealed tube, gave a base,  $C_4H_{11}N$ , and an acid,  $C_{14}H_{23}O_2$ . The authors prepared crude spilanthal (about 1%) from the air-dried flower-heads of the plant by Gerber's method. When kept it is changed into a resinous substance, and it becomes less soluble in ether. The base,  $C_4H_{11}N$ , formed by heating it with alcoholic hydrochloric acid, proved to be *isobutylamine*. Another decomposition product polymerised to a resinous substance. By shaking crude spilanthal in acetic acid solution in presence of platinum-black, it absorbs hydrogen gradually, with formation of *hydrosilanthal*; this is a colourless, viscous liquid with hay-like odour and bitter taste, which solidifies to crystals, m. p.  $28^\circ$ , is stable towards permanganate, and does not polymerise. It is probably a mixture of two substances,  $C_{13}H_{22}ON$  and  $C_{14}H_{23}ON$ . By heating with alcoholic hydrogen chloride in a sealed tube, hydrosilanthal yields *isobutylamine* and a saturated fatty acid, m. p.  $28^\circ$  and b. p.  $136$ — $140^\circ$  4 mm.; probably a mixture of decocic acid, m. p.  $31^\circ$ , and nonoic acid, m. p.  $12.5^\circ$ .

K. K.

**The Toxicity of Iron and the Antitoxic Properties of Copper with Respect to Ferrous Salts.** L. MAQUENNE and E. DEMOULLY (*Compt. rend.*, 1920, **171**, 218—222).—Ferrous salts are much more injurious to young plants than ferric salts. Any condition which tends to facilitate the oxidation of the ferrous to ferric salt consequently diminishes the toxicity of ferrous salts. This is the case with an addition of monopotassium phosphate, and particularly with an addition of copper sulphate, which has been

shown to exert a catalytic action on the oxidation of ferrous salts (compare this vol., ii, 547). W. G.

**Comparative Study of the Microflora and Nitrogen Content of Soils Partly Sterilised by Calcium Sulphide.**

G. TRUFFAUT and N. BEZSONOFF (*Compt. rend.*, 1920, **171**, 268-271).—With a strong application of calcium sulphide and naphthalene or cymene to soil in porous pots, without a crop, this aerobic medium favours losses of ammoniacal nitrogen and is unfavourable to the development of anaërobic bacteria, such as *Bacillus butyricus*. If the experiment is repeated with a crop present, there is much less loss of nitrogen, whilst if the application is applied to soil in the field, crops being grown, it is found that there is a large increase in growth on the treated plot, no loss of nitrogen from the soil, and a considerable increase in the numbers of *B. butyricus* present. W. G.

**Measure of the Ammonising Power of Arable Soil.**

R. PEROTTI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 251-256. Compare A., 1908, ii, 124).—The best conditions for carrying out the solution method of determining the ammonising power of arable soil are as follows: 10 c.c. of 1·5% peptone solution are treated in a test-tube with 5 c.c. of the solution, obtained by steeping 50 grams of the soil in 500 c.c. of well-water. The tube is kept in a thermostat at 20-25° for four days, after which the ammonia produced is estimated by distilling the contents of the tube in presence of magnesium oxide. The mean of four separate determinations is taken. T. H. P.

**The Mechanism of the Decomposition of Cyanamide in the Soil.** G. A. COWIE (*J. Agric. Sci.*, 1920, **10**, 163-176. Compare A., 1919, i, 376).—Cyanamide decomposes, in untreated soil or in soils previously heated to 120° or 135°, by a purely chemical change to carbamide. The subsequent conversion of the carbamide to ammonia is brought about by soil organisms. In sterile soils there is an accumulation of the carbamide, and this may also occur to a certain extent in soils under normal conditions. This decomposition of cyanamide appears to be more rapid in clay soils than in sandy soils. In the case of an inert sand, in which the cyanamide did not undergo decomposition, it was found that the addition of a zeolite, prehnite, resulted in the conversion of the cyanamide into carbamide.

Cyanamide does not appear to decompose in the manner indicated above in peat and fen soils; in these it gives rise to a relatively small production of carbamide under normal conditions. W. G.

**Solid Phases obtained by the Evaporation of certain Soil Extracts.** M. S. ANDERSON and WILLIAM H. FREY (*J. Ind. Eng. Chem.*, 1920, **12**, 663-668).—The salts deposited on the evaporation of the water extract of soils are of a much more complicated character than is indicated by a simple statement of the ions

existing in solution. The deposited salts are similar to those obtained by natural or artificial evaporation of sea-water, but no soil can be expected to furnish all the salts occurring in natural deposits of saline substances, since these represent crystallisation from a composite soil extract. As the salts begin to separate from the water extract at a point not far from the concentration corresponding with the moisture in an air-dry soil, it follows that the roots of growing plants may be in contact with solutions of these salts. Obversely, it is probable that the complex salts may be present in the soils only in solution in soil moisture, and never in the solid phase.

W. P. S.

**Substances Dissolved in Rain and Snow.** ANON (*Chem. News*, 1920, 121, 13-14. Compare Schutt and Dorrance, A., 1919, i, 116).—An account of analyses of rain and snow which fell in Mt. Vernon, Iowa, over the period October 9th, 1919, to May 22nd, 1920. During this period, 11.37 inches of rain fell and snow equivalent to 2.07 inches of rain, this in twenty-one precipitations of rain and eight of snow. Mt. Vernon is a town of 2,500 inhabitants, and is situated seventeen miles from the nearest industrial centre; it has no manufacturing industries. The analyses show that, during the period mentioned, 51.0306 lb. of sulphate as  $\text{SO}_4$  fell per acre, the largest amount being 34 parts per million of water on March 4th, or 7.7137 lb. per acre. The total amount of chlorine was 48.1644 lb. per acre, equal to 79.36 lb. of sodium chloride. The largest concentration was in a slight snow storm, equivalent to 0.02 inch of rain, on December 2nd, when 17.7 parts per million were obtained, which is equivalent to 4.0157 lb. per acre. Nitrogen was determined in four forms: as nitrates ( $\text{NO}_3$ ), nitrites ( $\text{NO}_2$ ), free ammonia, and albuminoid ammonia. A total of 0.62841 lb. of nitrogen as nitrate fell, the greatest amount being 0.3 part per million, or 0.06806 lb. per acre, on December 2nd and January 23rd, at which times snow equivalent to 0.08 inch and 0.59 inch of rain fell, respectively. As nitrite, there was a total of 0.03725 lb. per acre, of nitrogen, the greatest amount being on March 19th, equal to 0.02 part per million of water, or 0.00453 lb. per acre; at this time 0.4 inch of rain fell. Free ammonia, equivalent to 2.8642 lb. of nitrogen, fell during the period; on March 4th, nitrogen as ammonia, equal to 2.30 parts per million, or 0.52181 lb. per acre, fell, with 0.4 inch of rain. Albuminoid ammonia was less frequent in its occurrence, for 32% of the rainfalls gave no reactions for this form. A total of 0.4974 lb. of nitrogen as ammonia in the albuminoid form fell, the greatest single amount coming on February 12th, when 1.12 parts of nitrogen per million, or 0.2541 lb. per acre, fell, with snow equal to 0.25 inch of rain. The total amount of nitrogen as free and albuminoid ammonia was 3.3616 lb. per acre. The total amount of nitrogen in all forms was 4.02726 lb. per acre, and of this, 82.5% was in the form of the two ammonias. J. F. S.

## General and Physical Chemistry.

**Arc and Spark Spectra and the Periodic System.** INGO W. D. HACKH (*Astrophys. J.*, 1918, **48**, 241—255).—A survey of the relations among number and intensity of lines in the arc and spark spectra and the *E.M.F.* and valency of elements. It is shown that elements of high electro-potential give few lines, elements of weak electro-potential give many lines, and that elements with a low polar number (1—3) show very intense lines, whilst those with a high polar number (above 5) show lines of weak intensity. The spectrum is thus not the result of a number of homogeneous atoms, but the average result of different atoms or atom species. Thus the elements with strong *E.M.F.* have few species of atoms, the electrons being arranged in a few definite positions, whilst elements of weak *E.M.F.* have many species, the electrons being arranged in a variety of systems. The paper contains also a spiral arrangement of the periodic system from which the new periodic table is derived (A., 1918, ii, 306, 396).

CHEMICAL ABSTRACTS.

**Spectrum of Hydrogen Positive Rays.** G. P. THOMSON (*Phil. Mag.*, 1920, [vi], **40**, 240—247).—The positive ray spectrum of hydrogen has been examined under varying conditions in the discharge tube, whereby the proportion of atoms and molecules was varied over a wide range. The experiments show that the Balmer series is produced when positively charged hydrogen atoms pass through hydrogen as positive rays. The second spectrum is produced when positively charged hydrogen molecules pass through hydrogen as positive rays. The failure of Stark and Wilson to find the Döppler effect for the second spectrum of hydrogen is probably to be explained by the absence of molecules in the positive rays used. In certain circumstances a great change can be made in the nature of the positive rays given by a discharge tube by subjecting it to a magnetic field.

J. F. S.

**Krypton and Xenon.** J. N. COLLIE (*Proc. Roy. Soc.*, 1920, [1], **97**, 349—354).—A number of hitherto unmeasured lines have been observed in the spectra of xenon and krypton. The lines are observed with a fairly strong discharge, but still more are visible when a Leyden jar is placed in the circuit. It was found impossible to photograph the lines, which were therefore directly measured. In the case of xenon, 44 lines are recorded between  $\lambda\lambda$  7121 and 6036, and with krypton 35 lines between  $\lambda\lambda$  6768 and 5718 are measured. The lines are all of low intensity, but in the case of one experiment with xenon with a jar discharge the following brilliant lines were

seen:  $\lambda\lambda$  6880 (5), 6730 (5), 6669 (5), 6470 (7), 6318 (8), 6179 (8). It was observed that after passing a heavy current for some hours the xenon entirely disappeared and the tube became vacuous. This occurred with krypton and hydrogen, but with the difference that in the latter cases the gas was regained when the metal splashes were heated, whilst with xenon no gas could be recovered on heating the tube, electrodes, or splashes. The disappearance of the xenon occurs most readily with platinum electrodes, and aluminium and copper come next. No gas is evolved when the splashes are dissolved in acid or alkali, consequently there is no formation of a compound corresponding with a hydride, unless this, on treatment with alkali, forms an alkali xenate.

J. F. S.

**Revision of the Series in the Spectrum of Barium.**  
F. A. SAUNDERS (*Astrophys. J.*, 1920, 51, 23-36).—A study of photographs taken by A. S. King of vacuum furnace spectra leads to the revision and extension of the known spectrum of barium.

CHEMICAL ABSTRACTS.

**Character of the Absorption Spectra Produced by the Electric Furnace. II. The Zeeman Effect for Electric Furnace Spectra. III. Electric Furnace Spectra of Cobalt, Nickel, Barium, Strontium, and Calcium in the Region of Greater Wave-length.** ARTHUR S. KING (*Astrophys. J.*, 1920, 51, 13-22, 107-120, 179-186).—I. By placing a plug of graphite in the middle of a vacuum tube furnace a continuous spectrum depending on the temperature was produced with which the pure absorption spectra of barium, calcium, cobalt, iron, and titanium were studied. Those lines which are most intense in emission spectra were not always the strongest in absorption spectra. The absorption at each temperature stage corresponded with the emission spectrum several hundred degrees lower. By placing the plug beyond the middle of the furnace mixed spectra were obtained which should help to explain stellar spectra containing both bright and dark lines. II. The Zeeman effect noted in spark spectra has been closely checked by a study of the vacuum furnace emission and absorption spectra of iron in a magnetic field. III. The infra-red spectra for cobalt, nickel, barium, strontium, and calcium are tabulated. The lines that appear in the arc spectra above a certain minimum intensity usually appear in the furnace spectra, but not always in the same relative strength. The rules that hold for the visible spectrum as to change in intensity of the lines with temperature change hold for the infra-red.

CHEMICAL ABSTRACTS.

**Absorption Spectra of the Nitric Esters of Glycerol.**  
ELLIOT QUINCY ADAMS (*J. Amer. Chem. Soc.*, 1920, 42, 1321-1327).—A theoretical consideration of the work of Hepworth (T., 1919, 115, 810). It is shown that in plotting absorption spectra the use of the logarithm of the specific or molecular extinction-coefficient should be avoided, since it tends to obscure the rela-

tionship between absorption and constitution. The designations  $\alpha$  and  $\beta$ - applied by Will (A., 1908, i, 384) to the two mononitrates derived from glycerol should be interchanged. It is possible that the "glycidnitrat" described by Nef (A., 1905, i, 3) is glyceryl orthonitrate. The absorption spectra of the nitric esters of glycerol as given by Hepworth (*loc. cit.*) can be completely accounted for on the assumption that each nitrate radicle has an absorptive effect dependent on its location in the molecule, but independent of the presence or absence of other nitrate radicles. The absorptive effect of the nitrate radicle is about 1.5 times as great when it replaces the  $\beta$ -hydroxyl of glycerol as when it replaces an  $\alpha$ -hydroxyl group

J. F. S.

**Dissociation of Iodine Vapour and its Fluorescence.** ST. LANDAU and ED. STENZ (*Phil. Mag.*, 1920, [vi], 40, 189-197).—The fluorescence of iodine vapour at low pressure has been examined with the object of ascertaining the effect of temperature and dissociation on it. It is shown that raising the temperature does not produce as great an effect on the fluorescence of iodine vapour as has hitherto been thought. Fluorescence has been observed at temperatures above 800°. Dissociation destroys both the fluorescence and the resonance spectra. Thus the complicated vibrating system, corresponding with thousands of absorption lines in the visible part of the spectrum, is not inherent in the atom, but in the molecule. The structure of the atom should therefore be relatively simple. This idea is perfectly in accord with other facts obtained from a study of the fluorescence of vapours. It appears nearly certain that the absorption lines, which are so characteristic for diatomic iodine and so sensitive to the action of monochromatic light, do not belong to the absorption spectrum of monatomic iodine. J. F. S.

**Radiating Potentials of Nitrogen.** H. D. SWITH (*Physical Rev.*, 1919, **14**, 409-426).—The author has derived an equation for making accurate corrections for the distribution of velocities among the impacting electrons which are used to obtain radiating potentials. This correction applied to the results obtained on the radiating potentials of nitrogen has given the following values: at  $8.29 \pm 0.04$  volts a strong resonance, at 7.3 volts a doubtful resonance, at  $6.29 \pm 0.06$  volts strong resonance at low pressures. The first value is probably connected to the Lyman doublet wave-lengths 1492.8 and 1498.8 Å.U. by the relationship  $P.D. \times q = h v$ . The author finds some difficulty in identifying the other potentials accurately with nitrogen lines. On an assumption identifying the last resonance potential (that is, at 6.29 volts) with a line of wave-length from 2000 to 3000 Å.U. coming from neutral atoms, it is estimated that the upper limit for the heat of dissociation of the nitrogen mol. is 190,000 cals. per gram-mol.

CHEMICAL ABSTRACTS.

**The Relative Activity of Radium and the Uranium with which it is in Radioactive Equilibrium.** J. H. L. JOHNSTONE and B. B. BOLTWOOD (*Phil. Mag.*, 1920, [vi], **40**, 50-67).—A re-

determination of the ratio of the  $\alpha$ -activity of uranium, in equilibrium with its disintegration products, to that of the uranium (U I and U II) alone gave 4.73, in good agreement with Boltwood's first value, 4.69. The comparison was made with very thin films of the material, and in the case of the mineral, which was a selected specimen of uraninite from Spruce Pine containing 73% of uranium, the result was corrected for loss of emanation, and for thorium (1.9%  $\text{ThO}_2$ ) present. The ratio of the  $\alpha$ -activity of the radium itself to the uranium in the mineral was found to be 0.488, as compared with the first value, 0.45, and is far lower than the value, 0.57, deduced from the two-thirds power of the range of the respective  $\alpha$ -rays emitted, if the transformations involved were simple and direct. However, the first ratio, 4.73, is in excellent agreement with the value so calculated on the experimental datum that the branch actinium series contributes 0.28 to it. The last corresponds with a proportion of 8% of the uranium forming actinium and 92% radium. Now the two schemes proposed by Soddy and Cranston (A., 1918, ii, 211) for the origin of the actinium series require a ratio 0.55 and 0.53, according as the branch occurs at U I or U II, instead of the experimental value 0.488 already cited, if the actinium branch is 8%. Or, for the experimental value to be accounted for, an actinium branch of 26 or 14% respectively is required. Various possibilities are discussed without clearing up the discrepancy (compare Hahn and Meitner, this vol., ii, 147). F. S.

**Resonance and Ionisation Potentials for Electrons in the Monatomic Gases, Argon, Neon and Helium.** H. C. RENTSCHLER (*Physical Rev.*, 1929, **14**, 503-515).—With special precautions for eliminating impurities from the electrodes the author, using two methods (that of Tate and one similar to Lenard's first method), determined the resonance and ionisation potentials for argon, neon, and helium. He found ionisation potentials for helium to be about 26 volts, for neon about 19.5 volts, and for argon about 17 volts. Resonance potentials were only observed for the case of argon at about 12 volts. The accuracy of the values found is not great, as no correction was made for the initial velocities of the electrons.

CHEMICAL ABSTRACTS.

**Ionisation and Resonance Potentials for Electrons in Vapours of Lead and Calcium.** F. L. MOLLER, PAUL D. FOOTE, and H. F. STRIMSON (*Phil. Mag.*, 1920, [vi], **40**, 73-79).—The metal is boiled at low pressure in a tube containing a Wehnelt cathode surrounded by a cylindrical grid and a plate, a variable potential to accelerate the electrons being applied between the cathode and the grid, and a small retarding field between the grid and the plate. A sudden increase in the electron current leaving the cathode as the accelerating potential is increased shows when the ionisation point is reached. The "partial current," grid to plate, decreases when the electrons near the grid lose their velocity by inelastic collisions, as is the case when the velocity

exceeds the resonance potential. For lead, a mean value of 1.26 volts for the resonance potential and 7.93 volts for the ionisation potential was obtained, which, by the quantum relation, correspond with wave-lengths 9800 Å. and 1550 Å. For calcium, two resonance potentials, at 1.90 and 2.85 volts, were found, the first being more prominent, and an ionisation potential of 6.01 volts. These are associated with the wave-lengths 6572.78 Å. (1.877 volts), 4226.73 Å. (2.918 volts), and 2027.56 Å. (6.081 volts). F. S.

**Electrical Conductivity of Mixtures of Salts in the Fused and Solid States.** C. SANDONNINI (*Gazzetta*, 1920, 50, i, 289—321).—Using the arrangement devised by Kohlrausch, the author has measured the electrical conductivities of various binary mixtures of salts belonging to each of the three groups: (1) mixtures the components of which are miscible in the fused, and, maybe, also in the solid, state, but do not combine; (2) mixtures forming compounds decomposed on fusion; (3) mixtures forming one or more compounds stable in the fused condition. The systems examined were: (1)  $\text{PbCl}_2$ — $\text{PbBr}_2$ ,  $\text{AgCl}$ — $\text{AgBr}$ ,  $\text{NaNO}_3$ — $\text{KNO}_3$ ,  $\text{NaCl}$ — $\text{KCl}$ , (2)  $\text{AgCl}$ — $\text{TiCl}_3$ ,  $\text{NaCl}$ — $\text{CaCl}_2$ , (3)  $\text{AgNO}_3$ — $\text{TiNO}_3$ ,  $\text{KCl}$ — $\text{CaCl}_2$ ,  $\text{TiCl}_3$ — $\text{CdCl}_2$ ,  $\text{KCl}$ — $\text{CdCl}_2$ .

The conductivities of the fused mixtures are in all cases found to be lower than the values calculated from the law of mixtures. With certain pairs, the conductivity isotherms exhibit minima, this occurring principally when the components combine. Such minima do not, however, correspond always with the compounds formed, and with the system  $\text{NaCl}$ — $\text{CaCl}_2$  a minimum conductivity occurs at a temperature at which, according to thermal analysis, the compound formed by the two salts is completely dissociated, and at a composition far different from that of the compound.

From the values of the specific conductivity alone, certain deductions cannot be drawn, since variations of volume taking place during reciprocal dissolution of the two salts result in variation of the ionic concentrations. The author has therefore determined the densities of the following typical fused mixtures of salts:  $\text{NaNO}_3$ — $\text{KNO}_3$ ,  $\text{NaCl}$ — $\text{KCl}$ ,  $\text{NaCl}$ — $\text{CaCl}_2$ , and  $\text{KCl}$ — $\text{CaCl}_2$ . In these cases, the variation in specific gravity occurring during mixing is very small, even when the presence of complex molecules in the fused mass may be assumed.

The equivalent conductivities for these mixtures have been calculated, the changes in density being taken into account. With those pairs of salts for which compounds exist in the fused mass, the differences between the observed and calculated conductivities are certainly the more marked, but the isotherms in general exhibit no singular points corresponding with the compositions of the compounds, although with  $\text{KCl}$ — $\text{CaCl}_2$  this is approximately the case.

Conductivity measurements have also been made on the following solid mixtures:  $\text{PbCl}_2$ — $\text{PbBr}_2$ ,  $\text{AgCl}$ — $\text{AgBr}$ , and  $\text{AgCl}$ — $\text{TiCl}_3$ . The results obtained show that, when the solidified salt mixtures

consist of solid solutions which may be regarded as perfectly homogeneous, the phenomena encountered with mixtures of aqueous solutions or of fused salts having a common ion are repeated, the electrical conductivity being less than the calculated value. For the system  $TiCl_3$ - $AgCl$ , the conductivity curve exhibits a maximum coincident with the eutectic concentration (compare Benrath, A., 1909, ii, 12; Benrath and Wainoff, A., 1911, ii, 847), whereas the formation of solid solutions being excluded in this system, the presence in the mass of a double salt should produce a diminution, and not an increase, in the conductivity. The probable cause of this increase lies in a diminution of the internal friction which, for a given isotherm, will be the lower as the temperature approaches more nearly the melting point.

T. H. P.

**The Rectifying Contact Galena-metal. Artificial Sensitisation and Different Remarks.** C. FLORISSON (*Compt. rend.*, 1920, **171**, 106-108).—Artificial sensitisation produces the rectification *B* in specimens of galena having a slight original rectification *A*. Various methods of promoting this change were examined. The metal used for the contact is platinum. Heating in an atmosphere of nitrogen has, as a rule, no effect, although in a few cases the rectification *B* was produced. The action of air at high temperature not only did not produce the rectification *B*, but tended to destroy it in specimens where it was apparent. The action of pure dry sulphur dioxide was very irregular, but sulphur vapour in a current of nitrogen almost invariably caused marked sensitisation. Selenium was similar, but much less marked in its action. In all these cases where sensitisation occurred, a very thin superficial layer was apparently produced, which probably contained more sulphur than lead sulphide, the sulphur being present either in combination or in solid solution. The presence of this layer in naturally occurring sensitive galena is discussed.

W. G.

**Anode Corrosion of Lead in Sodium Hydroxide Solutions.** O. W. BROWN, C. O. HENKE, and L. T. SMITH (*J. Physical Chem.*, 1920, **24**, 367-379).—The corrosion of lead anodes during the electrolysis of solutions of sodium hydroxide of various concentrations has been examined at 20°, 60°, and 75°, using current strengths of various values and an *E.M.F.* of about 3 volts. It is shown that the amount of corrosion increases rapidly with increasing temperature; thus, using a solution of 152 grams of sodium hydroxide per litre, the amount of corrosion is 4.5% of the theoretical at 20°, 98.3% at 60°, and theoretical at 75°. At all temperatures, the corrosion increases with increasing concentration of sodium hydroxide to a maximum, which is reached at 152 grams per litre, and then falls, with a further increase in concentration. Thus at 60° the following fractions of the theoretical amount of corrosion are observed with the given concentrations: 35 grams/litre, 5.7%; 71 grams/litre, 49.3%; 110 grams/litre, 96.4%; 152 grams/litre, 98.3%; 192 grams/litre, 58.5%; 220 grams/litre,

61.5%; and 304 grams/litre, 37.7%. The current efficiency increases rapidly with increase of temperature; this is especially marked where the concentration is 152 grams/litre and the current density 4 amperes/sq. cm. The discharge potentials and the total polarisation have been determined for various current densities at 75° for a solution containing 152 grams/litre. It is found that there is 100% corrosion when the bath tension is low (0.2—0.3 volt), and a low corrosion when the voltage is high, 3.2. The total polarisation increases from -0.179 volt with a current density 1.56 amperes/sq. cm. to -2.484 volts with 4.22 amperes/sq. cm. When the anode is corroding properly, the discharge potential is about 0.2 volt, but when it ceases corroding, the discharge potential rises to -1.317 volts.

J. F. S.

**Ballo-electricity, Molecular Forces, and Electrical Forces.**

J. TRAUBE (*Ann. Physik*, 1920, [iv], 62, 165—172. Compare Christiansen, A., 1919, ii, 385).—A theoretical paper in which the author considers the results of Christiansen's work. It is shown that the ballo-electric charge of solutions runs parallel with the surface tension; aballistic substances are shown to be without effect on the surface tension, whilst cataballistic and anaballistic substances have considerable influence on the surface tension of the solvent. In the case of homologous series of organic acids and bases, it is shown that there is a continuous increase in the surface tension and the ballo-electric charge of the solutions with increasing molecular weight. It is shown that the molecular forces and the forces of cohesion, like the chemical affinity, are electrical in origin.

J. F. S.

**Mobility of the Electrolytic Ions.** M. BORN (*Zeitsch. Physik.*, 1920, 1, 221—249).—A mathematical paper. An expression is deduced for calculating the radii of the ions. The radii of the alkali metal ions and the halogen ions have been calculated to be somewhat less than  $10^{-8}$  cm. It is further shown that the magnitude of the radius increases with the atomic number of the atom from which the ion is formed, and, for the same atomic number, that the radius increases with the magnitude of the charge carried by the ion.

CHEMICAL ABSTRACTS.

**Magnetic Susceptibilities of Quartz, Tellurium, and some Holmium Compounds.** GILLIS WISTRAND (*Diss. Uppsala*, 1916, 56 pages).—Samples to be tested were fastened to a glass plate which could be moved in and out of a magnetic field produced by two Ruhmkorff coils. The effect of forces acting on the samples was determined by weighing. The sample was hung by a fine copper wire, 1 metre long, to the underside of the pan of a precision balance, the sample hanging free between the electromagnetic poles. Samples investigated were two clear quartz cylinders about 10 cm. long, and practically free from iron, a bar of tellurium about 4 cm. long, commercial samples of ferric hydroxide, manganese dioxide and manganese sulphide, and ferric oxide, made by

heating ferric hydroxide; holmium oxide was tested in three fractions, because of the varying presence of other rare metals; the nitrate and chloride were also investigated. Similar determinations for comparison were made on water in a thin glass tube. The author found the specific magnetic susceptibility ( $x_s$ ) of water corrected for air to be  $-0.7260 \times 10^{-6}$ , for quartz in vacuum  $-1.070 \times 10^{-6}$ , for tellurium  $-1.70 \times 10^{-6}$ , for ferric hydroxide  $193.8 \times 10^{-6}$ , for ferric oxide  $60.7 \times 10^{-6}$ , for manganese dioxide  $37.3 \times 10^{-6}$ , and  $64.80 \times 10^{-6}$  for manganese sulphide.  $x_s = +132.6 \times 10^{-6}$  and  $+172.0 \times 10^{-6}$  for holmium nitrate and chloride respectively, which gave 51.4 as the value of the "magneton" number of holmium.  $x_s = +243 \times 10^{-6}$  was the average of the three fractions of holmium oxide, the fractions giving 51.4, 50.7, and 51.5, respectively, as the magneton numbers.

## CHEMICAL ABSTRACTS.

**Calorimetric Method for Standardising Thermometers by Electrical Energy.** THEODORE W. RICHARDS and SETSUE TAMARU (*J. Amer. Chem. Soc.*, 1920, **42**, 1374-1377).—Thermometers may be standardised by immersing them in a calorimeter containing a known amount of water at a measured temperature, and adding measured amounts of heat by allowing a known electric current of suitable voltage through a definite resistance to enter the liquid, thus adding a measured quantity of electrical energy. The rise of temperature can then be calculated and compared with the temperature registered by the thermometer. This method is capable of giving results of the greatest accuracy. As an example of the method, a measured quantity of electrical energy was added nine times in succession to a calorimeter (adiabatic) containing a Beckmann thermometer. The readings were  $2.0503^\circ$ ,  $2.5555^\circ$ ,  $3.0510^\circ$ ,  $3.5475^\circ$ ,  $4.0410^\circ$ ,  $4.5375^\circ$ ,  $5.0320^\circ$ ,  $5.5225^\circ$ , and  $6.0080^\circ$ . Allowing for the difference of specific heat of water, the error in the thermometer is found to be  $-0.0102^\circ$  between  $2.55$  and  $3.05$ .  
J. F. S.

**The Expansion of Saturated Vapours.** G. BRUHAT (*Compt. rend.*, 1920, **171**, 162-164).—A mathematical discussion of the subject.  
W. G.

**Specific Heat of Saturated Vapours and Entropy-temperature Diagrams of Fluids.** ALFRED W. PORTER (*Phil. Mag.*, 1920, [vi], **40**, 211-212).—The author discusses some points in a paper under the above title by Ewing (this vol., ii, 412). It is shown the specific heat of the saturated vapour in the case of sulphur dioxide can be positive, and that the inversion temperatures are  $97.5^\circ$  and  $114^\circ$ . The entropy of a liquid is not  $f/C_p \cdot dT/T$ , where  $C_p$  is the specific heat at constant pressure, even with the proviso that the value of  $C_p$  must be taken at saturation. The value of  $C_p$  must be replaced by  $K_v$ , the specific heat of saturated liquid. The difference between  $C_p$  and  $K_v$  is negligible at temperatures suffi-

ciently remote from the critical temperature, but it tends towards  $\infty$  as the critical temperature is approached. The relation between the two quantities is  $K_w = C_p - T(\delta v/\delta T)_p \cdot dp/dT$ , or, in terms of the specific heat at constant volume ( $C_v$ ), it may be expressed  $K_w = C_v - T(\delta p/\delta T)_v / (\delta p/\delta T)_r \cdot ds/dT$ , where  $s$  is the specific volume of the liquid at saturation. The values of  $K_w$  for sulphur dioxide are given for the range  $-20^\circ$  to  $155.5^\circ$ , and it is shown that  $K_w$  is not a linear function of the temperature even in regions remote from the critical region.

J. F. S.

**Method of Suppressing the Correction of Temperature in the Determination of Melting-points.** MAURICE FRANÇOIS (*Bull. Soc. chim.*, 1920, [iv], 27, 528-536).—The apparatus used is a long-necked flask having two side-tubes, one near the bulb and the other being the continuation of the neck of the flask. These two side-tubes are joined by a vertical tube, which is continued upwards and expanded into a bulb. The flask and vertical tube are filled with oil to just above where the elongated neck joins the vertical tube. The material under examination is placed at the closed end of a long capillary tube, which is then bent back on itself. This tube is attached to the bulb of a thermometer, which is then placed in the vertical tube connected with the flask, the scale of the thermometer thus being in the oil. By this means a correction for exposed stem is avoided. A simple arrangement of mirrors is described by means of which it is possible to read the thermometer and observe the material in the melting-point tube simultaneously through one telescope.

W. G.

**Estimation of Impurities by means of the Melting-point Curve.** WALTER P. WHITE (*J. Physical Chem.*, 1920, 24, 393-416).—A theoretical discussion, accompanied by practical examples of methods of determining melting points and the estimation of impurities from the melting-point curves. It is shown that freezing points are more accurately determined by immersing the thermometer in the substance than by the capillary tube method. If, in addition, the form of the freezing-point curve is observed, an indication of the amount of impurity present is obtained, which is independent of all previous knowledge or uncertainty as to the melting point of the pure substance and even of the absolute accuracy of the thermometer. If the determinations are a control of a purification process, there is also a saving of time and the avoidance of certain chances of error. Smallness of dimensions of the melting tube diminishes local temperature differences, and is very often a superior substitute of the stirring rod. It also economises both time and material. A small thermocouple or cell of several couples is very useful with small test samples. The complications, usually almost negligible, arising from specific heat, uneven temperature, and other causes are considered, and suitable experimental arrangements are suggested for removing them.

J. F. S.

**Reduced Transition and Freezing Points.** J. NARBUTT (*Physikal Zeitsch.*, 1920, **21**, 341—349).—A mathematical paper, in which a number of relationships between the transition temperatures and melting points of substances respectively are deduced. It is shown that at similar reduced temperatures the ratio between the transition affinity or the fusion affinity and the heat of transition or the heat of fusion of substances at the transition temperature or the melting point,  $\Theta$ , respectively is the same for all substances,  $A'_r/U'_\Theta = A''_r/U''_\Theta$ . The ratio between the transition or fusion affinity and the transition or fusion temperature,  $\Theta$ , for similar reduced temperatures is the same for all substances with the same entropy value,  $S_\Theta$ .  $A'_r/\Theta' = A''_r/\Theta''$ . A similar relationship exists between the heat of transition or the heat of fusion and the corresponding temperature,  $U'_r/\Theta' = U''_r/\Theta''$ . The heat of fusion or transition may be calculated from the vapour pressure of the supercooled liquid or solid substance, or that of the labile and stable modifications by means of the formula

$$U_\Theta = 2R\Theta\phi(1-\phi^2) \cdot \log_e p_2/p_1.$$

The vapour-pressure curves of a supercooled liquid may be deduced if the vapour-pressure curve of the solid is known or vice versa. The ratio of the vapour pressure of the supercooled liquid and solid or the labile and stable modifications of a substance at the same reduced temperature is the same for all substances,  $p_2'/p_1' = p_2''/p_1''$ . At similar reduced temperatures the relationship  $\sqrt[p_2']{p_1'} = \sqrt[p_2'']{p_1''}$  holds for supercooled and solid substances or for the labile and stable modifications of a substance. The formulae have been applied to the known data for benzene, water, and the halogen derivatives of benzene, and shown to hold very exactly. J. F. S.

**Practical Method of Determining the Boiling Point, with Small Amounts of Substance.** VICTOR ARRUGUINE (*Soc. Chim. Argent.*, **3**, 133 [reprint]).—The apparatus consists essentially of a small test-tube, 80—85 mm. long and 9 mm. in diameter, having a loose inner tube open at one end and a bulb at the other end, being about 5 mm. in diameter and 52—51 mm. long. This inner tube is first filled with mercury to within 1 mm. of the top, and the liquid under examination is added. This tube is inverted into mercury in the test-tube, which is then filled with glass beads and closed with a metal cap. The whole apparatus is placed against the bulb of a thermometer and slowly heated in a bath of a suitable liquid. The temperature is read on the thermometer, when the mercury is at the same level in the test-tube and the inner tube. Certain corrections, all very small in amount, must be made for the vapour pressure of mercury and for the error produced by excess of liquid in the inner tube. Formulae are given for calculating these. The method is only applicable for liquids having boiling points below 210°. W. G.

**Spontaneous Evaporation.** HARRY B. WEISER and EVERETT E. PORTER (*J. Physical Chem.*, 1920, **24**, 333—341).—The present paper records the results of a repetition of some of Babington's

experiments (*Proc. Roy. Soc.*, 1859, **10**, 132) on the spontaneous evaporation of solutions. In this paper it was stated that solutions of potassium ferrocyanide, potassium tartrate, copper sulphate, and potassium chlorate evaporated more rapidly than pure water under the same conditions. A number of experiments have been made with solutions of these substances of various concentrations, and the rate of evaporation determined. It is shown that to obtain reproducible results the containers must be scrupulously clean, and that they must be slowly rotated on a revolving platform. Crystallisation must all take place on the base of the dish, and there must be no creeping. It is shown that in all cases, even with saturated solutions, the evaporation is slower than with pure water. Taking the precautions mentioned, this method may be used for obtaining a fairly accurate measurement of the relative lowering of the vapour pressure of various substances. A number of comparison experiments on the evaporation of solutions of sulphuric acid and chromium trioxide indicate that the latter exists in dilute solution chiefly as dichromic acid, as was pointed out by Ostwald from other considerations.

J. F. S.

**Vapour Pressures of certain Substances: Chloropicrin, Cyanogen Bromide, Methyl dichloroarsine, Phenyl dichloroarsine, Diphenylchloroarsine, and Arsenic Trichloride.** G. P. BAXTER, F. K. BEZZENBERGER, and C. H. WILSON (*J. Amer. Chem. Soc.*, 1920, **42**, 1386-1393).—The vapour pressures of the substances named in the title have been determined at a series of temperatures by the air current method, except in the case of arsenic trichloride at higher temperatures, where the static method was employed. The vapour pressure in all the cases can be expressed by a formula of the type  $\log p = A + B/(273 + t)$ ; values of  $A$  and  $B$  have been deduced in each case. The following equations and values actually measured have been obtained: chloropicrin,  $\log p = 8.2424 - 2045.1/273 + t$ ;  $-20^\circ$ , 1.50 mm.;  $-19^\circ$ , 1.70 mm.;  $-18^\circ$ , 1.90 mm.;  $0^\circ$ , 5.71 mm.;  $10^\circ$ , 10.37 mm.;  $15^\circ$ , 13.82 mm.;  $20^\circ$ , 18.31 mm.;  $25^\circ$ , 23.81 mm.;  $30^\circ$ , 31.10 mm.;  $35^\circ$ , 40.14 mm.; cyanogen bromide,  $\log p = 10.3282 - 2457.5/273 + t$ ;  $-17.3^\circ$ , 5.9 mm.;  $-15.5^\circ$ , 6.3 mm.;  $0^\circ$ , 21.2 mm.;  $15^\circ$ , 63.3 mm.;  $25^\circ$ , 119.5 mm.;  $35^\circ$ , 223.5 mm.; methyl dichloroarsine,  $\log p = 8.6944 - 2281.7/273 + t$ ;  $-17^\circ$ , 0.60 mm.;  $-16^\circ$ , 0.61 mm.;  $-15^\circ$ , 0.71 mm.;  $0^\circ$ , 2.17 mm.;  $15^\circ$ , 5.91 mm.;  $25^\circ$ , 10.90 mm.;  $35^\circ$ , 19.33 mm.; phenyl dichloroarsine,  $\log p = 9.150 - 3164/273 + t$ ;  $0^\circ$ , 0.004 mm.;  $15^\circ$ , 0.014 mm.;  $25^\circ$ , 0.035 mm.;  $35^\circ$ , 0.076 mm.;  $45^\circ$ , 0.159 mm.; diphenylchloroarsine,  $\log p = 7.8930 - 3288/273 + t$ ;  $25^\circ$ , 0.0003 mm.;  $45^\circ$ , 0.0039 mm.;  $55^\circ$ , 0.0063 mm.;  $65^\circ$ , 0.0148 mm.;  $75^\circ$ , 0.0282 mm.; arsenic trichloride,  $\log p = 7.5183 - 1720/241.2 + t$ ;  $0^\circ$ , 2.44 mm.;  $25^\circ$ , 11.63 mm.;  $35^\circ$ , 19.53 mm.;  $50^\circ$ , 40.90 mm.;  $60^\circ$ , 64 mm.;  $70^\circ$ , 97 mm.;  $80^\circ$ , 145 mm.;  $90^\circ$ , 211 mm.;  $100^\circ$ , 301 mm. The following heats of vaporisation have been calculated by means of the Clausius-Clapeyron formula,

$$L = T \cdot dp/dt(V_{\text{liq}} - V_{\text{vap. soln}}).$$

Chloropicrin, 35°, 6.77; 0°, 7.10; cyanogen bromide, 35°, 8.08; 0°, 8.60; arsenic trichloride, 100°, 6.86; 50°, 7.29; 0°, 7.42. An accuracy of a few per cent is claimed for the numerical values.

J. F. S.

**Determination of the Last of the Three Functions which Define the Equation of State of Ethyl Ether.** E. ARRIÉS (*Compt. rend.*, 1920, **171**, 154—156).—The values of the functions  $x$  and  $\Phi$ , which define the equation of state of ethyl ether (compare this vol., i. 418), have been determined, and it is necessary only to determine the values of  $a$  for the equations  $v_1 = RT_{c,r}(a+y_1)/8P_c\Phi$  and  $v_2 = RT_{c,r}(a+y_2)/8P_c\Phi$ . Using the values obtained experimentally by Young for the liquid state, it is possible to calculate the numerical values of  $a$  for each 10° and to find an expression which represents this function:

$$a = a_c + (1 - \tau)^2/10^6,$$

where  $\Theta = (A + Br + Cr^2 + Dr^3) \cdot 0.0073688$  and the value of  $a_c$  is given by  $v_c = RT_c(a_c + 2)/8P_c$ , which gives  $a_c = 0.09809$ .

The results calculated from these formulae are in close agreement with those found experimentally by Young. W. G.

**Equation of State.** M. P. APPLEBEY and D. L. CHAPMAN (*Phil. Mag.*, 1920, [vi], **40**, 197—200).—The mean kinetic energy of translation of a molecule can no longer be assumed to be proportional to the temperature, and consequently the dynamical definition of temperature must be abandoned. From this point of view the authors deduce a new equation of state. They start with the assumption “that in a closed space which contains a large number of similar molecules the ratio of the number of molecules per unit volume whose potential energy is  $J$  to the number of molecules per unit volume whose potential energy is zero is given by the expression  $e^{-J/kT}$ , in which  $k$  is the gas constant for a single molecule and  $T$  the thermodynamic temperature.” The final form of the equation deduced is  $[Ph'(e^{Ph'/kT} - 1)] + Ph'/2 \cdot \frac{2}{3}mV^2/2$ , in which  $m$  is the mass of a single molecule of the gas and  $V$  the volume of fluid displaced by the molecule. J. F. S.

**Equation of Condition.** C. DIETERICI (*Ann. Physik*, 1920, [iv], **62**, 75—94). A theoretical paper, in which the author considers the pressure isothermal obtained by Young (A., 1899, ii, 633) for isopentane and by Amagat (A., 1893, ii, 152) for carbon dioxide. It is shown that the difference between the ideal saturation work,  $J_{id} = RT \log r_2/r_1$ , and the actual work,  $J_{act} = p_s(r_2 - r_1)$ , is given by the expression  $(a - RTc_k)(S_1 - S_2)$ , in which  $S_1$  and  $S_2$  are the saturation densities and  $a$  a constant which is determined by the critical data alone. J. F. S.

**Correspondence of Substances in the Solid State.** FÉLIX MICHAUD (*Compt. rend.*, 1920, **171**, 241—243).—The law of corresponding states has been generalised by making coincide certain

homologous points instead of the critical points (compare Curie, *Arch. Sci. phys. nat.*, 1891, 26), and taking as specific units the co-ordinates of these points. There exists such a point in the solid region which is particularly useful. It has been shown that the specific heat,  $C$ , tends towards zero as the absolute temperature,  $T$ , approaches zero. Consequently,  $C/T=0$  when  $T=0$ , and it also tends towards zero for  $T=\infty$ , and in consequence it must pass necessarily through a maximum, and it is this point, where the temperature is  $T_m$ , that is taken as a centre of correspondence. Thus the law of Dulong and Petit is only exact when the substances are taken in their corresponding states, as just defined, that is, at the absolute temperatures proportional to the temperatures  $T_m$ . It further results that the atomic entropies, at temperatures proportional to the temperatures  $T_m$ , are equal. These facts are demonstrated in the cases of aluminium, silver, copper, lead, and zinc.

W. G.

**Calorimetric Procedure for Determining the Heat of Slow Reactions. I. Analysis of Partially Concurrent Heat Effects.** FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1920, 42, 1295—1308).—A theoretical paper in which the method of extrapolating, from a time-temperature change curve of two concurrent reactions, the temperature change of a single process is developed. In the case of the inversion of sucrose by acid, the heat changes are two: (1) heat of solution of the solid sucrose in the acid solution, and (2) heat of inversion. This case is considered as well as the cases where there is concurrent heat reaction in the same sense, that is, both exothermic or both endothermic, and concurrent heat reactions in opposite senses, as in the case of sucrose and dilute acid. Equations are developed whereby extrapolation of the desired heat change may be made from the experimental curves.

J. F. S.

**Thermochemistry of Hydrocarbons according to P. W. Zubov's Data.** W. SWIETOSLAWSKI (*J. Amer. Chem. Soc.*, 1920, 42, 1312—1321).—A theoretical paper in which the values recalculated by the author from Zubov's data (*loc. cit.*) are critically examined. By analysis of the equations for the combustion of hydrocarbons, the terms  $(y+w-2z)=Y$  and  $(x+w-z-w)=X$  are obtained, which correspond respectively with the heats of combustion of the linkings C—C and C—H;  $y$  is the heat of formation of the atomic linking C—C,  $x$  that of C—H,  $2w$  the heat of formation of the molecule O<sub>2</sub>,  $4z$  that of CO<sub>2</sub>, and  $2w$  that of H<sub>2</sub>O. The terms  $X$  and  $Y$  are termed the thermochemical characteristics of the C—C and C—H linkings respectively. These characteristics have remarkably constant values in the case of *n*-hexane, *n*-octane, *n*-decane, *cyclohexane*, and naphthalene. Hence, if the molecule of naphthalene contains the double bond C=C, the heat of formation of this double bond is exactly the same as that of two single bonds, C—C. The value of  $X$  and  $Y$  for

methane and ethane are exactly the same as in the cases mentioned above. The following values of the thermochemical characteristics  $X$  and  $Y$  and of the homologous difference  $Z$  are  $X = -53.72$  cal.,  $Y = -52.25$  cal.,  $Z = 2X + Y = -157.77$  cal. In spite of the proved constancy of  $X$  and  $Y$  in five saturated, one polymethylene, and one aromatic hydrocarbon, they are shown to vary in other hydrocarbons. It is definitely established that the heat of formation of the C-C linking increases with the increase of the number of carbon atoms in the polymethylene hydrocarbons, and that the heat of formation of the same linking is increased by the replacement of a hydrogen atom by a methyl or a *n*-propyl group. The increase in  $Y$  is not considerable. In the case of the polymethylene hydrocarbons, it varies between  $-0.5$  and  $+0.5$  in the series *cyclopentane*, *cyclohexane*, *cycloheptane*. It varies within the limits  $-0.8$  and  $+1.7$  when one, two, or three methyl groups are introduced in the molecule of the polymethylene hydrocarbons. The analysis of the data on unsaturated hydrocarbons shows the important difference  $2(y - y_2)$  between the heat of formation of two single linkings, C-C, and that of the double one, C=C. This difference, due to the change of constitution of the hydrocarbon examined, varies within the very large limits,  $+8.0$  cal. to  $+1.0$  cal. In special cases it is possible that  $2(y - y_2)$  can be equal to zero, for example, in the case of naphthalene. J. F. S.

**Static Friction. II.** W. B. HARDY (*Phil. Mag.*, 1920, [vi], **40**, 201-210. Compare *ibid.*, 1919, [vi], **38**, 32).—The relationship between chemical constitution and the lubrication of bismuth has been examined at  $11-14^\circ$  by measuring the static friction between a burnished bi-muth surface and bismuth slider, 70.5 grams weight and 25.5 mm. radius of curvature, lubricated by a large number of pure organic substances, which included thirteen alcohols, ten acids, two ketones, six esters, nine hydrocarbons, all of these of the aliphatic series, and forty-five cyclic compounds. It is shown that static friction is a function of the molecular weight of the lubricant, and in a simple series of chain compounds, such as fatty acids, alcohols, or paraffins, a good lubricant will be found if the series is taken high enough. It is by no means a simple function; the friction, for example, rises sharply in moving from chloroform to carbon tetrachloride, and from phenol to quinol and catechol. The influence of molecular weight is overshadowed by constitution. A linear relationship is found in the series benzene, naphthalene, anthracene, the paraffins, and ammonia-propylamine. In the aliphatic acids and alcohols, the linear relation to molecular weight is disturbed by the weighting of the chain at one end by the  $-CO_2H$  and  $-OH$  groups respectively. In a simple chemical series, lubrication and viscosity change in much the same way with molecular weight, but there is no fundamental relation between viscosity and lubrication. The curves for acids, alcohols, and paraffins show no break where, with increasing molecular weight, the lubricant becomes a solid at the temperature of observation.

as is shown by the pairs, benzene-naphthalene, menthone-menthol, thymol-carvacrol. The upward trend of the first part of the curve for the aliphatic alcohols is in agreement with the fact that methyl alcohol is abnormal in some of its physical properties. In their qualities as lubricants of bismuth, ring compounds are the converse of chain compounds; thus, the effect of a double bond is to decrease the lubricating value of the former and increase that of the latter. On the other hand, the presence of unsaturated atoms increases the lubricating qualities of chain compounds, whether it be the double-bonded oxygen of ketones or acids, or carbon of olefines and alcohols, but this rule is departed from in the case of acids when the chain becomes much elongated. When a ring and chain are joined, as in butylxylene, the product is a better lubricant than either constituent. When the atoms are disposed with complete symmetry about a carbon atom, the compound is a very bad lubricant, as is seen in the case of carbon tetrachloride and pentaerythritol,  $C(CH_2OH)_4$ . In the ring compounds, the replacement of hydrogen decreases lubricating power in the case of N, O, or  $-CO_2H$ , and increases it in the case of other groups in the order  $C_3H_5 < C_4H_8 < OH$ . The effect of a second group of the same or of a different kind is to decrease the effect of the first, and the simpler the group the more effective it is. Esters occupy an unexpected position. The aliphatic esters are much worse lubricants than their related acids or alcohols. Hydroxy-acids have a remarkably good lubricating power in the aliphatic series, but this is entirely lost in cyclic compounds. Generally, it is noted that no cyclic compound is a good lubricant. It is also shown that the better a lubricant is, the more strongly is it adsorbed by a metal surface.

J. F. S.

**Adsorption by Charcoal. I. Relation of Service Time to Adsorption and Absorption.** H. H. LOWRY and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 1393-1408).—The adsorption of nitrogen, carbon dioxide, and water by a large number of different varieties of charcoal has been studied. It is shown that no relationship exists between the length of time the charcoal has been in use and the adsorption for gases, such as nitrogen and carbon dioxide. Differences in the method of preparation of the charcoal change the adsorptive capacity by as much as 100%. Nitrogen and carbon dioxide adsorbed by charcoal may be regarded as a condensed layer one molecule thick. Measurements of the isothermal adsorption of water at  $25^\circ$  show that there is no adsorption in the strict sense of the term, but that the water is held in the capillary tubes, that is, it is absorbed. Using Anderson's formula (A., 1914, ii, 632) connecting the radius of a capillary with vapour pressure, the mean diameters of the capillaries of four specimens of charcoal have been calculated, and are found to vary from  $2.8 \times 10^{-7}$  cm. to  $9.2 \times 10^{-7}$  cm. The maximum diameter of any of the charcoal examined was  $1.3 \times 10^{-6}$  cm. By means of the same formula and the absorption isothermals of

water, the surface of the charcoal is found to vary from 160 sq. metres to 436 sq. metres per gram. The variation of surface is not always accompanied by a corresponding variation in adsorptive capacity. This makes the conception of elementary spaces, as postulated by Langmuir, a necessity. There is no relationship between the volume of the capillaries and the time of use of the charcoal. The same is also true for the saturation point and the retentivity of the charcoal.

J. F. S.

**Adsorption by Charcoal. II. Relation of Oxygen to Charcoal.** H. H. LOWRY and G. A. HULETT (*J. Amer. Chem. Soc.*, 1920, **42**, 1408-1419. Compare preceding abstract).—The adsorption of oxygen by charcoal has been examined with several varieties of charcoal. In the case of this gas, the behaviour is shown to be anomalous, due to the coupling of two phenomena, adsorption and surface combination. Charcoal has been heated in a furnace up to 1200° out of contact with oxygen-containing materials, and the evolved gases collected and analysed. The results point to the formation on the charcoal surface of a carbon-oxygen complex, which is essentially a stable solid oxide of carbon, at ordinary temperatures. This complex decomposes on heating into carbon monoxide and carbon dioxide, and can thus be considered to be an intermediate compound in the combustion of charcoal. This is supported by the views of Armstrong (A., 1904, ii, 948) and by the experimental work of Rhead and Wheeler (T., 1912, 101, 831; **103**, 461), and by Langmuir (A., 1915, ii, 467). The amount of oxygen thus found to be combined in charcoal has been found to vary in two samples from 1.71% and 3.75% of the initial weight of the charcoal.

J. F. S.

**Solubility. II. Solubility Ratios of Salts in Strong Homoiionic Solvents.** J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1920, **42**, 1448-1454. Compare this vol., ii, 294).—The solubility of potassium chloride, bromide, iodide, nitrate, chlorate, and iodate has been determined at 20° in solutions of potassium hydroxide of concentrations varying between 1.71*N* and 15.02*N*. The solubility of the haloids and the chlorate steadily decreases with increasing concentration of the hydroxide, that of the nitrate remains constant at the higher concentrations of hydroxide after decreasing with increasing hydroxide concentration, whilst the iodate decreases to an hydroxide concentration 11.10*N*, and then increases to 14.85*N*. The results are considered in the light of the views put forward in an earlier paper (*loc. cit.*). It is found that, taking the salts in pairs, the ratio of the solubility products is constant over a considerable range of hydroxide concentration, except in the case of the nitrate-chlorate ratio. The results indicate that the nitrate, chlorate, and iodate ions are equally hydrated. The salts investigated fall into groups: (1) the haloids and (2) the oxygen salts. The salts in either group exhibit similar behaviour as solutes, and are similarly hydrated and equally acted

on by electric forces in the solvent over a wide range of concentrations.

J. F. S.

**Hypophosphorous Acid. I. Its Ionisation Equilibria.**  
ALEC DUNCAN MITCHELL (T., 1920, 117, 957—963).

**Polarity and Ionisation from the Point of View of the Lewis Theory of Valency.** WENDELL M. LATIMER and WORTH H. RODEBUSH (*J. Amer. Chem. Soc.*, 1920, **42**, 1419—1433).—A theoretical paper in which the conceptions of polarity and the ionisation of polar and non-polar compounds are considered on the basis of Lewis's valency hypothesis (A., 1916, ii, 310). Salts of elements which are not polar are ionised in solution by reacting with the solvent molecules or other molecules. The properties of an ionising solvent depend on the existence of moderately strong intermolecular fields. The dielectric constant is a measure of this type of polarity, but it has no significance with regard to highly polar compounds.

J. F. S.

**The Crystal Lattice.** A. REIS (*Zeitsch. Physik.*, 1920, **1**, 204—220).—A method based on a pure geometrical conception of the space lattice is put forward to answer the questions of the nature of the existence of molecules and radicles in the crystal lattice. Application of this method to chemical compounds shows that a fundamental difference exists between the space lattice of salts and compounds not exhibiting a salt-like character. For chemical and crystallographic problems the method has many applications. It is shown that the distances between atoms in molecules and radicle ions are appreciably smaller than those between molecules. Classification of the kinds of lattices has been found to produce a homogeneous picture of the relation which exists between chemical constitution and cohesion forces, whilst the differences between these classes are readily shown by a consideration of the compressibility, hardness, and thermal expansion. The cohesion forces in all states of aggregation, as well as the association forces in liquids, are essentially the same, and result from pure electrostatic influences of the molecule. Those optical properties of salts which correspond with the mutual linking of ions are associated with the state of aggregation, whilst all other optical properties are independent of it. Both the heat of transition of polymorphous modifications and the heat of sublimation are distinctly less for molecular lattices than for ion lattices. In ion lattices, and only in these, the molecular union is raised and displaced by the lattice union.

CHEMICAL ABSTRACTS.

**Arrangement of Atoms in Crystals.** W. LAWRENCE BRAGG (*Phil. Mag.*, 1920, [vi], **40**, 169—189).—An examination of the distances between neighbouring atoms in a crystal leads to an empirical relation determining these distances. The distance between the centres of two atoms may be expressed as the sum

of two constants characteristic of the atoms. The arrangement of the atoms in a crystalline structure may therefore be pictured as that of an assemblage of spheres of appropriate diameters, each sphere being held in place by contact with its neighbours. This empirical law is summarised in a curve, in which the constants for a number of elements are plotted against the atomic numbers. The curve is periodic, and resembles Lothar Meyer's curve of atomic volumes. Each atom occupies a constant space in any crystalline structure of which it forms part. The space occupied by the alkali metals and the metals of the alkaline earths is greatest, that occupied by the halogens and electronegative elements least. The accuracy of the relationship is discussed. Variations of the order of 10% between the calculated and observed distances occur, so that the law is only approximately true. Nevertheless, it is of considerable assistance in the analysis of the more complex crystal structures, since the conception of the atoms as an assemblage of spheres of known diameters packed tightly together limits the number of possible arrangements which have to be tried in interpreting the diffraction of  $\text{X}$  rays by the crystal. The physical significance of the relation is examined with reference to Langmuir's theory of atomic structure. From this point of view, it follows that two electronegative atoms are situated close together in a crystalline structure because they share electrons, and the spheres representing them are therefore assigned small diameters. On the other hand, an electropositive element does not share the electrons in its outer shell with neighbouring atoms, and is therefore situated at a distance from other atoms, so that it appears to occupy a greater space in the structure. It is shown that the relationship is less accurate when applied to the crystals of metals, which, on Langmuir's theory, consist of an assemblage of positive ions held together by electrons which have no fixed positions in the structure. From the distance between electronegative atoms holding electrons in common, an estimate is made of the diameter of the outer electron shell of the inert gases. The following values are given: neon 1.30 Å., argon 2.05 Å., krypton 2.35 Å., and xenon 2.70 Å. The atomic diameter of some thirty-eight elements is given, and the distance between the atoms in a large number of crystals.

J. F. S.

**Rate of Change of Distribution of Particles in a Colloidal System.** A. WESTGREN (*Arkiv. Mat. Astron. Fysik*, 1918, 13, No. 14, 18 pp.).—An experimental verification of Smoluchowski's formula for the rate of change of concentration of particles in a colloidal system,  $\Delta^{-2} = 2rP$ , in which  $P = (4/\alpha\pi)$

$$\int_{-\infty}^{\infty} dR \int_{-\infty}^{\infty} dr \left[ \frac{N_a}{(e^{-R^2 - r^2 + 2RTt} / \sqrt{1 - t^2})} \right] RrdR$$

$\alpha = a^2/4Dt$ , and, according to Einstein,  $D = (RT/N)(1/6\pi\eta r)$ . This formula permits a determination of Avogadro's constant which leads to  $N = 6.0 \times 10^{22}$ , with a probable error of 5%.

CHEMICAL ABSTRACTS.

**Distribution of Acetic Acid between Water and Charcoal.** ALWYN PICKLES (*Chem. News*, 1920, **121**, 49).—When acetic acid solutions are treated with charcoal, a large proportion of the acid is rapidly removed, but several hours are required for complete equilibrium to be attained. Relatively more acid is removed from dilute solutions, and the concentration of the acid in mols. per c.c. of charcoal varies with the kind of charcoal and its state of division. An increase of temperature over a long period, so that the surface and interior effects are complete, reduces the acid concentration of the charcoal, but over a short period increases it, owing to the acceleration of the still incomplete interior effect. Animal charcoal is an exception, since it removes the acid almost entirely by adsorption. In applying the distribution equation,  $\frac{C_n \text{ Charcoal}}{C \text{ Water}} = K$ , the values of  $n$  giving the most consistent values for  $K$  ranged from 1.76 to 2.6. The value for  $n$  (2.35) in Thorpe's "Dictionary of Applied Chemistry," vol. ii. (colloids), thus appears to be an average value. C. A. M.

**Equilibrium between Chlorine, Plumbous Chloride, and Plumbic Chloride in Aqueous Solution.** ERNEST W. WESCOTT (*J. Amer. Chem. Soc.*, 1920, **42**, 1335–1349).—The equilibrium between solid plumbous chloride and chlorine in hydrochloric acid has been investigated with acid of concentrations down to the point where lead dioxide separates as a solid phase. The results show that the complex chloroplumbic acid has the composition  $\text{HPbCl}_6$ , for with a given chlorine pressure the quantity of this complex acid present in equilibrium with solid plumbous chloride was found to be proportional to the first power of the chloride-ion concentration. The hydrogen-ion concentration, which would not be involved in the equilibrium if the ionisation of the substances was complete, was found to have a small secondary effect, probably owing to an influence on the ionisation of the chloroplumbic acid. The equilibrium constant corresponding with the expression  $(\text{PbCl}_6^{\prime})/(\text{Cl}^{\prime}) \cdot p_{\text{Cl}}$  is given by the expression  $K' = 0.055 + 0.07c_n$ , the concentrations being expressed in mols. per 1000 grams of water, the partial pressure of chlorine being given in atmospheres and the ionisations of hydrochloric acid and chloroplumbic acid being assumed equal. The equilibrium constant of the reaction  $\text{PbCl}_2(s) + \text{Cl}_2(g) + 2\text{H}_2\text{O} = \text{PbO}_2(s) + 4\text{H}^{\prime} + 4\text{Cl}^{\prime}$ , as given by the expression  $K = (\text{H}^{\prime})^4 \cdot (\text{Cl}^{\prime})^4 / p_{\text{Cl}}$ , was found to be  $2.4 \times 10^{-8}$ , under the assumption that the ionisation of the hydrochloric acid and the chloroplumbic acid is complete. From these equilibrium constants and from other data found in the literature, the values of the decrease of free energy at  $25^{\circ}$  were calculated for the case that the concentrations of all dissolved substances are molecular, except that of chlorine, the partial pressure of which is one atmosphere, and were found to be those expressed by the following free energy equations:  $\text{PbCl}_2(s) + \text{Cl}_2(g) + \text{Cl}^{\prime} = \text{PbCl}_3^{\prime} - 6590$  joules,  $\text{PbCl}_2(s) + 2\text{H}_2\text{O} + \text{Cl}_2(g) = \text{PbO}_2(s) + 4\text{H}^{\prime} + 4\text{Cl}^{\prime} - 43.500$  joules, and  $\text{Pb}(s) + \text{O}_2(g) = \text{PbO}_2(s) + 219,000$  joules. J. F. S.

**The Kinetic Theory of Gases in the Light of the Theory of Relativity.** RUDOLF MEWES (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1920, **12**, 33—34; from *Chem. Zentr.*, 1920, iii, 70—71).—A connexion has not yet been established between the kinetic theory of gases or its laws and the theory of relativity developed by Lorentz, Gerber, Einstein, and Minkowski. The author's previous experiments and new calculations open the possibility of developing a dynamic theory of gases and vapours on the basis of the general law of action of mass. H. W.

**Magnitude of the Atom.** A. LANDÉ (*Zeitsch. Physik*, 1920, **1**, 191—197).—A theoretical paper on the sphere of influence of the electrons. It is stated that the radius of the second electron ring of atoms having an atomic number in the neighbourhood of 10 is approximately  $0.35 \times 10^{-8}$  cm. Values are given for the lattice constant,  $\delta - 2r_+ + 2r_-$ , for a number of alkali haloids. Here  $r_+$  and  $r_-$  are the radii of the positive alkali- and the negative halogen-ions (or better of their spheres of influence). The following first approximations have been deduced for the diameters of the spheres of influence of a number of ions:

Na..	K..	Rb..	Cs..	F..	Cl..	Br..	I..
$2r \times 10^8 = 2.2$	2.9	3.3	3.2	2.4	3.3	3.6	4.1

It is shown that  $r_+ / r_- = 0.68$  for eight electrons and  $= 0.51$  for four electrons. That the value for the ratio for eight electrons is smaller than that calculated from the series of numbers given above, is explained on the ground that in the lattice the large halogen-ion spheres are more compressed than in the smaller alkali-ion spheres.

#### CHEMICAL ABSTRACTS.

**New Periodic Relationship between the Atomic Weights of the Chemical Elements. II. Law of Mirror Image Remainders.** KARL FEURLE (*Physikal. Zeitsch.*, 1920, **21**, 382—385. Compare this vol., ii, 303).—In a previous communication (*loc. cit.*) the author determined the difference between the ideal atomic weight and the actual atomic weight for the elements with atomic numbers 1—37. In the present paper the elements with atomic numbers 38—71 have been treated in the same way. The author now plots the differences as ordinates against the atomic numbers as abscisse, and obtains an irregular curve which can be divided by a line at atomic number 37 into two halves which are exact mirror images of one another, that is, where a maximum is found in the first half of the curve, a minimum occurs in the same relative position in the second half of the curve and vice versa. It is shown that by means of this relationship doubtful atomic weight values may be checked and corrected. J. F. S.

**General Isotopy.** A. VAN DEN BROEK (*Physikal. Zeitsch.*, 1920, **21**, 337—340).—A theoretical paper, in which the general relationships of isotopes are discussed. It is shown that if the periodic

system were a system of only two series, for example,  $3+4n$  and  $4n$ , without nucleus electrons, then atomic weight =  $2Z$  and  $2Z+1$  respectively, and all atomic weights would be whole numbers ( $Z$  is the atomic number). That this is not so is conditioned in the first place by the existence of at least two other series,  $1+4n$  and  $2+4n$ , the atoms of which are less common. A table is drawn up of the whole of the elements on the basis of the above-named four series, and a system of isotopes on the  $4\alpha/2\beta$  hypothesis is given for the elements with atomic numbers 29 to 35.

J. F. S.

**Nuclear Constitution of Atoms.** Sir E. RUTHERFORD (*Proc. Roy. Soc.*, 1920, [4], 97, 374-400).—Bakerian lecture. A general discussion of previously published work on the constitution of the lighter atoms. Structures are put forward for carbon, nitrogen, and oxygen atoms.

J. F. S.

**A Force, apparently due to Mass, Acting on an Electron, and the Non-identity of Isotopes in Spectra and other Properties.** WILLIAM D. HARKINS and LESTER ARONBERG (*J. Amer. Chem. Soc.*, 1920, **42**, 1328-1335).—A theoretical paper, in which the nature of isotopes is discussed. It is shown that isotopes may be distinguished by their spectra, and that there must be some difference, although small, between the other properties of isotopes.

J. F. S.

**Glass to Metal Joints.** E. C. MCKELVY and C. S. TAYLOR (*J. Amer. Chem. Soc.*, 1920, **42**, 1364-1377).—A résumé of the various metal glass joints described in the literature is given, and this is followed by a description of the method of making trustworthy joints between metal and glass. Two types of joint are described: (a) soldered joints, (b) fused joints. The first type of joint has only been used for joining tubes. A length of glass tube chosen so that it will fit easily inside the metal tube, is roughened for a length of 15-20 mm. and then coated with platinum by covering it with a suspension of platinum chloride in oil of lavender, and then burning off carefully in a bunsen flame. The metal tube is carefully coated with tin, solder, or lead. Using a slightly acid solution of zinc chloride as soldering flux, the metal tube is heated so that the tin is molten and the hot glass tube inserted and the whole allowed to cool slowly. Fused joints are made between metal and glass by means of the Kraus flux (equal weights of zinc oxide, borax, and powdered soda glass fused together). The metal tube is covered on its interior with a thin layer of the flux, the glass tube is flared out to a flat ring of a width equal to three times the thickness of the glass wall, and while hot pressed into the flux-lined metal tube. Fusion is completed by heating the outside of the metal tube in such a way that the glass is kept cool enough to prevent deformation. An account is given of the various types of apparatus for which these joints are applicable.

J. F. S.

**Equipment for Drying Ovens.** C. W. FOULK (*J. Amer. Chem. Soc.*, 1920, **42**, 1454—1455).—The drying space in ovens is considerably augmented by removing the door and placing a number (three or four) drawers on each shelf, so that the whole oven space is filled with these easily removed drawers. The bottoms of the drawers are made of metal gauze, and the ease of use makes the back of the oven as convenient of access as the front. J. F. S.

**Washing Bottles in Gas Works Laboratory Practice.** H. J. HAILSTONE (*Gas World*, 1920, **72**, 376).—The inlet tube reaches to the bottom of the bottle and terminates in an upturned jet. Around it is a spiral tube, its lower end fitting over and being supported by the jet. An aperture should be left between the lower end of the spiral tube and the point of the jet, and for this purpose the lower end of the spiral tube is flattened, thus preventing the jet from completely closing the tube. In operation, the bottle is filled level with the top of the spiral with the solution, and the gas passed through it. The bubbles issue from the jet and ascend through the spiral carrying "plugs" of the solution with them, thus keeping the gas in contact with the liquid for a longer time. At the top of the spiral the gas passes out and the "plugs" of liquid fall back. Circulation of the liquid is thus made practically constant and the washing efficient. CHEMICAL ABSTRACTS.

**Apparatus for Ultrafiltration.** RICHARD GANS (*Ann. Physik*, 1920, [iv], **62**, 327—330).—An apparatus for rapid ultra-filtration is described. The principle of the present apparatus is the same as that of Bechhold (*Ann.*, 1908, **ii**, 24, 823), but the construction is much simpler. Collodion filters are conveniently prepared by treating 12.5 grams of gun-cotton with sufficient absolute alcohol to moisten it, and then making the volume up to 500 c.c. with ether. A little of the solution is poured evenly on a glass plate, and when the ether has evaporated it is plunged into water to remove the filter from the glass. The filter is then washed in running water, and may be preserved in water containing a little chloroform or formalin. A more rapid filter is obtained when equal volumes of alcohol and ether are used in the preparation. The permeability of a filter can be varied by the addition of glacial acetic acid, but the permeability does not depend entirely on the quantity of acetic acid used, but also on the time which has elapsed between its formation and its use. J. F. S.

### Inorganic Chemistry.

**Solubility of Iodine in Hydriodic, Hydrobromic, and Hydrochloric Acids, and Formation of the Corresponding Polyhalogenated Acids.** I. E. OLIVERI-MANDALÀ and A. ANGENICA (*Gazzetta*, 1920, **50**, **i**, 273—281).—The saturated

aqueous solution of iodine at 25° contains 0.0334% of iodine, or 0.00131 mol. per litre. The solubilities of iodine in solutions of various concentrations of hydriodic, hydrobromic, and hydrochloric acids have also been determined. It is found that the solubility of iodine in the halogen hydracid is equal to that in the solution of the corresponding potassium salt at the same concentration; the solubility of the iodine is hence specific to the halogen ion, and is independent of the nature of the positive ion of the halogen compound. The freezing points of hydriodic and hydrobromic acid solutions are unaltered by dissolution of iodine in these solutions. Further, if the existence of trihalogenated acids in dilute solution be assumed, it is found that the degree of dissociation of hydriodic acid in solutions of 0.1—0.3*N*-concentration is equal to that of the acid,  $HI_3$ ; the same holds for  $HBr$  and  $HBr_3$ . T. H. P.

**Distribution of Ozone in the Direct Current Corona.**  
 ERIC K. RIDEAL and JAKOB KUNZ (*J. Physical Chem.*, 1920, **24**, 379—392).—The formation of ozone by various methods is considered theoretically in the light of the various radiation hypotheses, and the conclusion is drawn that molecular species of a given type may be activated to varying degrees by a given radiation. The distribution of ozone in a direct-current corona is experimentally examined. The corona was produced in a brass tube with quartz ends, a platinum wire being suspended centrally down the tube and connected to the positive pole of a current of 16,500 volts, whilst the brass tube is earthed. Oxygen was slowly passed through the corona, and samples were withdrawn at various points and analysed. To control the analyses, an optical analysis was also carried out by means of a beam of ultraviolet light and a photoelectric cell. It is shown that the distribution of ozone in the corona varies very notably with the sign of the discharge, the negative corona producing higher concentrations than the positive corona. The average yield of ozone obtained was 0.045 gram/coulomb at the negative corona and 0.024 gram/coulomb at the positive corona. The distribution of ozone in a direct-current positive corona differs in a marked manner from that in a negative corona. The ultraviolet light emission from the corona exceeds that of the visible light, and in the corona itself the ratio of ultraviolet light to visible light is exceedingly high. J. F. S.

**Sulphur Dioxide as a Source of Volcanic Sulphur.** JACOB PARISH (*Proc. Indiana Acad. Sci.*, 1918, 170—171).—Sulphur dioxide is reduced to sulphur by methane at elevated temperature. The author suggests that sulphur occurring in volcanic regions may, in part, be formed by reduction of sulphur dioxide by methane, carbon monoxide, or hydrogen, all of which occur in volcanic exhalations.

## CHEMICAL ABSTRACTS.

**Freezing-point Solubility Curve for Sulphur and Dichlorodiethyl Sulphide.** J. A. WILKINSON, CHRIST NEILSON, and H. M. WYLDE (*J. Amer. Chem. Soc.*, 1920, **42**, 1377—1382).—The solubility of rhombic sulphur, monoclinic sulphur, and

amorphous sulphur has been determined in  $\beta\beta'$ -dichloroethyl sulphide over the temperature range 13.82–128°, and the solubility-freezing-point curves constructed. The solubility of rhombic and monoclinic sulphur is the same at all temperatures. Below 78°, the solid phase which crystallises is rhombic sulphur, whilst above that temperature monoclinic sulphur separates. The solubility of amorphous sulphur is less than 0.14% at temperatures below 120°. Saturated solutions of sulphur in dichloroethyl sulphide contain 7.6% of sulphur at 80°, 11.3% at 90°, 17.5% at 100°, and 21.0% at 104°.

J. F. S.

**The System Ammonia-Water.** S. POSTMA (*Rec. trav. chim.*, 1920, **39**, 515–536).—The melting-point curve of the system ammonia-water shows the existence of two hydrates,  $\text{NH}_3\text{H}_2\text{O}$  and  $2\text{NH}_3\text{H}_2\text{O}$ , having m. p.'s –79.0° and –78.8° respectively. The boiling-point curves do not give any indication of the existence of these compounds.

The vapour-pressure curve of ammonia was determined, and is represented by the formula  $\log p = 7.2379 - 1282.86/T$ , from which the heat of vaporisation is calculated as 5864 cal. The vapour-pressure curves of mixtures of ammonia and water were constructed, and also the curve of sublimation of solid ammonia.

W. G.

**Oxidation of Arsenious Anhydride in Alkaline Medium in the Presence of Ferrous Sulphate.** G. GIRZ (*Compt. rend.*, 1920, **171**, 174–176).—The absorption of oxygen by a solution of arsenious oxide and ferrous sulphate in the presence of sodium hydroxide varies with the amount of alkali present. The volume of oxygen absorbed at first diminishes as the amount of alkali increases, reaching a minimum when the alkali is slightly in excess of that required to form the arsenite,  $\text{Na}_2\text{As}_2\text{O}_4$ . It then increases to a constant maximum, when the amount of alkali present is slightly in excess of that required to form the arsenite,  $\text{Na}_2\text{As}_2\text{O}_4$ . If the amount of alkali present is kept constant, the oxygen absorbed is proportional to the amount of iron present, but is always in excess of that required to oxidise the ferrous salt to the ferric state.

W. G.

**Charcoal before the War. III.** WILDER D. BANCROFT (*J. Physical Chem.*, 1920, **24**, 342–366. Compare this vol., ii, 429).—A further discussion of the properties of charcoal. In the present paper, the oxidation of charcoal from various sources by various reagents is considered.

J. F. S.

**The Action of Extremely Finely Divided Gases.** C. ZENGHELIS (*Compt. rend.*, 1920, **171**, 167–170. Compare this vol., ii, 363).—A more detailed study of the reduction of carbon dioxide in the presence of water by hydrogen in a very finely divided state shows that the action steadily diminishes in velocity with the time. Although it takes place to some extent in the dark, it is markedly accelerated by sunlight, and still more so by

ultraviolet rays. In all cases, the formaldehyde first produced rapidly undergoes polymerisation. The reduction of carbon dioxide by hydrogen takes place slowly with both gases in solution in water without any passage of the hydrogen through a porous vessel.

W. G.

**Some Sources of Helium in the British Empire.** J. C. McLENNAN (*Bull. No. 31, Dept. of Mines, Canada*).—An account of the natural gases of Canada, British Columbia, New Zealand, New Brunswick, and England, which contain helium. The radioactivity and helium content are tabulated, and methods of estimation are described. [Compare *T.*, 1920, 117, 923; this vol., ii, 488, 508.]

J. F. S.

**Application of the Laue Diagram to the Determination of the Structure of Calc Spar.** ERNST SCHIEROLD (*Leipziger Abh.*, 1919, **36**, 65—213; from *Chem. Zentr.*, 1920, **iii**, 123).—The investigation was undertaken with the object of elucidating suitable methods of determining indices and of applying the Laue diagram to a useful means of determining structure. The systematic procedure recommended gives results confirmatory of Bragg's structure model when applied to sodium chloride. The structure deduced for calc spar permits a satisfactory explanation of the cleavage relationships from Bragg's model.

H. W.

**The Constituents Formed by Reciprocal Penetration of Zinc and Copper at a Temperature at which these Two Metals and all their Alloys are in the Solid State.** H. WEISS (*Compt. rend.*, 1920, **171**, 108—111).—When zinc and copper were heated in close contact at 400° for two days, the following constituents were found in the contact layer: pure zinc or its solid solution,  $\eta$ ; the constituent  $\epsilon$  to a thickness of about 0.2 mm.; the constituent  $\gamma$ , thickness about 1 mm.; a very thin zone of the constituent  $\beta$ ; and copper or its solid solution,  $\alpha$ . If the duration of heating was increased to ten days, the thickness of the zones  $\epsilon$  and  $\gamma$  increased without appreciable alteration of the zone  $\beta$ .

W. G.

**System Zinc Oxide, Phosphoric Oxide, and Water at 25° and 37°.** N. E. EBBLY, C. V. GROSS, and W. S. CROWELL (*J. Amer. Chem. Soc.*, 1920, **42**, 1433—1439).—The equilibrium between zinc oxide, phosphoric oxide, and water has been determined at 25° and 37° over a long range of concentrations, and the equilibrium curves have been constructed. At 25° the solid phases,  $Zn_3(PO_4)_2 \cdot 4H_2O$ ,  $ZnHPO_4 \cdot 3H_2O$ , and  $Zn(H_2PO_4)_2 \cdot 2H_2O$ , separate, whilst at 37° an additional solid phase,  $ZnHPO_4 \cdot H_2O$ , is obtained. The tetrahydrate of normal zinc orthophosphate may be prepared by saturating a 50% solution of phosphoric oxide in water with zinc oxide at the boiling point. The water lost by evaporation is replaced and the mixture cooled in ice. About 10 volumes

of ice-cold water are added, and the solution vigorously stirred and poured through a filter into a large porcelain dish. The dish and its contents are heated on a water-bath with stirring, when a large quantity of shining plates of the tetrahydrate separate.  $Zn_3(PO_4)_2 \cdot 4H_2O$  crystallises in shining, orthorhombic plates;  $ZnHPO_4 \cdot 3H_2O$  forms sticky, thread-like crystals which agglomerate into cotton-wool-like masses;  $ZnHPO_4 \cdot H_2O$  forms small, hard, transparent needles, which, since the extinction is oblique to the long axis, are probably triclinic;  $Zn(H_2PO_4)_2 \cdot 2H_2O$  forms large, transparent, triclinic rhombohedra. J. F. S.

**New Method of Preparing Tripotassium Lead Hydrogen Octafluoride.** FRANK C. MATHERS (*J. Amer. Chem. Soc.*, 1920, 42, 1309—1311. Compare Clark, A., 1919, ii, 513).—Lead peroxide is readily attacked by 96% hydrofluoric acid, and a yield of 62% of lead tetrafluoride obtained. On dilution of the solution, the tetrafluoride is speedily hydrolysed, but this may be largely prevented by the addition of a little potassium or ammonium fluoride before dilution. Tripotassium lead hydrogen octafluoride,  $3KF \cdot HF \cdot PbF_4$ , is best prepared by fusing a mixture of equal weights of potassium hydrogen fluoride and lead peroxide in a platinum dish at 200°. The fluoride is melted and the dioxide slowly added, and the heating continued until the mass becomes pasty. After cooling, the mass is moistened with concentrated hydrofluoric acid, stirred with a carbon rod, and heated at 220° for several hours: after repeating the heating several times, the mass becomes practically white and contains 80—86% of the octafluoride. Pure crystals were obtained by digesting the crude residue with concentrated hydrofluoric acid, filtering, and crystallising. The pure salt is very easily hydrolysed, but the presence of a small excess of potassium fluoride retards the hydrolysis to a marked degree. The action of heat on the octafluoride does not give enough fluorine for the odour to be recognised, although the platinum dish was etched. J. F. S.

**Crystal Structure of Ferromagnetic Metals.** ALBERT W. HULL (*Physical Rev.*, 1919, 14, 540—541).—Since the atoms of ferromagnetic materials are, in general, ferromagnetic only when in pure metallic condition and between definite limits of temperature, and the relative spacing of the atoms is apparently essential, it might have been anticipated that ferromagnetic metals would have the same crystal structure. That this is not the case is shown by the data on the type of lattice and the distance between atoms of chromium, iron, cobalt, and nickel (compare *ibid.*, 1917, 10, 661). Nickel has the same crystal structure as copper, whilst cobalt appears in two forms, one like copper and one like magnesium. Neither is like iron. Chromium, which is not ferromagnetic, has a centred cubic arrangement, like iron. It is evident, therefore, that ferromagnetism does not depend on any particular arrangement of atoms. It is much more likely that it depends on

the distance between the atoms, which would explain the fact that this property is lost when the temperature is increased beyond a definite value.

## CHEMICAL ABSTRACTS.

**Catalytic Action of Copper Salts on the Oxidation of Ferrous Compounds by Air.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1920, **171**, 65-69).—Copper salts exert a marked catalytic effect on ferrous salts, favouring their oxidation in air. This effect is noticeable at extreme dilutions (1 in 100,000,000), and is sensitive to the least change in the reaction of the medium. It is apparently independent of the degree of ionisation of the mixture of copper and ferrous salts, but is most marked with ferrous salts of weak acids, being apparently related to their degree of hydrolytic dissociation.

W. G.

**The Precipitation of Tin by Iron.** N. BOUMAN (*Rec. trav. chim.*, 1920, **39**, 537-541).—By the addition of a solution of stannous chloride, the potential of iron in a solution of ferrous chloride becomes less negative, so that it is then less electronegative than tin; consequently it is no longer in the state to precipitate tin from its solution. This result is discussed on the electronic theory, and a satisfactory explanation given. At the same time, it is shown that reduced iron will precipitate tin from its solution if boiled with a slightly acid solution of stannous chloride.

W. G.

**Zirconium.** J. W. MARDEN and M. N. RICH (*J. Ind. Eng. Chem.*, 1920, **12**, 651-656). Fairly pure (99.8%) zirconium oxide may be prepared from zirconite by decomposing the mineral with sulphuric acid, precipitating the zirconium as basic sulphate, and igniting the precipitate. Good yields are also obtained by fusing zirconite with sodium carbonate and hydroxide and precipitating zirconium oxide by means of sulphur dioxide, and by a method in which the zirconium is precipitated as phosphate. Potassium zirconium fluoride may be prepared in pure condition by dissolving zirconium dioxide in hydrofluoric acid, treating the solution with the calculated amount of potassium carbonate, and recrystallising the salt three times. Its solubility in water varies greatly with the temperature, 100 c.c. dissolving 25.0 grams at 100°, 15.0 grams at 18°, and 0.78 gram at 0°. The pure metal may be prepared from this salt or from the oxide. The coherent metal may be obtained by aluminothermic reduction, by heating the amorphous product, and (in admixture with carbide) by reducing zirconium oxide with carbon. The amorphous variety is obtained by reducing potassium zirconium fluoride by means of sodium or aluminium in an exhausted iron tube or a vacuum furnace. The coherent metal is much less chemically active than the amorphous variety, and, unlike the latter, is insoluble in all acids except aqua regia and hydrofluoric acid. A study of different analytical methods showed that zirconium is incompletely precipitated as fluoride, and that it is only quantitatively precipitated by peroxide when the concentra-

tion of the latter in the solution is high. The precipitation as phosphate is best effected in the presence of 10% of sulphuric acid, hydrogen peroxide being added to retain the titanium in solution. The quantity to be precipitated should not exceed 0.05—1 gram in 200 c.c., and the liquid should be heated to boiling point and allowed to remain after the addition of an excess of disodium hydrogen phosphate. In the case of solutions containing 10 to 20% of sulphuric acid, an excess of 50% of ammonium phosphate should be added. [See also *J. Soc. Chem. Ind.*, 1920, September.]

C. A. M.

**Thorium and Uranium Content of Certain Minerals; the Gradual Transformation of Thorium-B-Thorium-C.** STEFAN MEYER (*Sitzungsber. Akad. Wiss. Wien*, **128**, [2a], 897—908; from *Chem. Zentr.*, 1920, iii, 75).—The estimation of thorium or uranium in uranium ores containing very little thorium, or in thorium ores with a very small uranium content, cannot be effected by the usual methods; it is, however, relatively easy to estimate minimal amounts of uranium by the proportional radium content, and of thorium through its active precipitates. In a specimen of monazite sand, the ratio of thorium to uranium was 83:1, an extreme value, which is not commonly observed. A specimen of Joachimsthal pitch-blende contained  $6.61 \times 10^{-5}$  grams of thorium isotopes (thorium + ionium) for 1 gram of uranium, or  $3.33 \times 10^{-7}$  grams of radium. The thorium content of a crystalline Morogoro uranium mineral, the uranium content of which was already known, was estimated in the following manner. The amount of thorium-B obtained under definite conditions from a known weight of the mineral was compared with the amount produced under identical conditions from a mineral of known thorium content. The Morogoro mineral was thus found to contain 0.53% of thorium and 74.5% of uranium. The amount of thorium is so great that the equivalent of the thorium-ionium from the mineral can scarcely be distinguished from that of thorium itself. In an appendix, the author gives tables showing the effect of differing exposure in thorium emanation on the activity of active thorium precipitates. H. W.

**F Crystalline Structure of Antimony.** R. W. JAMES and NORMAN TUNSTALL (*Phil. Mag.*, 1920, [vi], **40**, 233—239).—The crystal structure of antimony has been determined for antimony by means of an X-ray spectrometer, using a bulb with a palladium anti-cathode. The glancing angles for first-order spectra were as follows: (100),  $50^{\circ}27'$ ; (110),  $70^{\circ}24'$ ; (110),  $70^{\circ}50'$ ; (111),  $40^{\circ}0'$ ; and (111),  $19^{\circ}14'$ . The intensities and the small glancing angle indicate that the underlying structure is a face-centred lattice, and that the unit rhomb contains eight atoms. The structure, as in the case of the diamond, consists of two interpenetrating face-centred lattices. The arrangement of the lattices can be seen, as follows. “Suppose for one of the lattices, diagonals are drawn parallel to the trigonal axis for each of the eight equal rhombo-

hedral cells into which the unit lattice may be divided. From considerations of symmetry, it is clear that the atoms of the second lattice must lie in these diagonals. If they lay at the unoccupied corners of the first lattice, the structure would become a simple rhombohedral one. This does not accord with the observed facts, but if the atoms of the second lattice are all displaced from these corners along the diagonals in the same direction by a distance equal to 0·074 of the length of the diagonal of one of the small cells, all the observed facts are explainable." J. F. S.

**Revision of the Atomic Weight of Bismuth. Analysis of Bismuth Chloride.** O. HÖNIGSCHMID and L. BIRKENBACH (*Sitzungsber. Akad. Wiss. München*, 1920, 83-86; from *Chem. Zentr.*, 1920, iii, 122).—With the object of discovering possible isotopes of bismuth, the authors have analysed and investigated bismuth chloride and bromide, using the methods of Richards and his co-workers. The ratio  $\text{BiCl}_3 : 3\text{AgCl}$  was determined gravimetrically, and the ratio  $\text{BiCl}_3 : 3\text{Ag}$  by gravimetric titration with the aid of the nephelometer. The first series gave the value  $\text{Bi} = 209\cdot024$ , whilst the second set indicated  $\text{Bi} = 209\cdot027$ ; the mean,  $209\cdot026$ , is regarded as the present most probable value for the atomic weight of bismuth, and is a unit higher than that previously adopted. H. W.

**[Salts with High Ammonia Content.]** WALTER PETERS (*Ber.*, 1920, **53**, [H], 1143).—The formation of amines containing more than six molecules of ammonia (Ephraim and Moser, this vol., ii, 378) has previously been observed by the author, who has obtained platinum double salts with 9, 12, 15, or 18 molecules (compare Peters, *A.*, 1910, ii, 114). H. W.

### Mineralogical Chemistry.

**Pulverulent Mineral [Fluorite] from Dorgali, Sardinia.** ENRICO CLERICI (*Atti R. Accad. Lincei*, 1920, [v], **29**, i, 309-312).—This mineral, which is shown by its physical and chemical properties to be fluorite, exhibits thermoluminescence, even under carbon tetrachloride or acetone, and emits radiations capable of influencing photographic plates and of penetrating glass, mica, or gelatin, but not aluminium or black paper. This phenomenon may be due to the presence of traces of rare earths. T. H. P.

**Plumbiferous Barytes from Shibukuro, Japan.** RYŌICHI ŌHASHI (*Min. Mag.*, 1920, **19**, 73-75).—The mineral is deposited

by a hot spring, the water of which has the following composition in parts per thousand: H 0.07500, K 0.02491, Na 0.04415, NH<sub>4</sub> 0.00011, Ca 0.04870, Mg 0.01483, Fe 0.24846, Al 0.09622, Cl 2.69729, H<sub>2</sub>SO<sub>4</sub> 0.42034, SO<sub>4</sub> 0.93776, HBO<sub>3</sub> 0.04244, H<sub>2</sub>SiO<sub>3</sub> 0.37022; total, 5.02043; D<sup>25</sup> 1.0030. In the rock fissures and at the orifice where the temperature is nearly 100°, the deposit consists of ordinary barytes, but in the stream of hot water, with a temperature of 40—50°, the crystalline deposit consists of plumbiferous barytes of the variety known as "hokutolite" (so named from the occurrence in the hot spring at Hokuto, in Formosa), together with sulphur, siliceous sinter, ferric oxide, realgar, and orpiment. It has the composition:

BaO.	PbO.	SO <sub>3</sub> .	Fe.	Ign.	Total.
I. 59.96	4.67	32.77	—	—	97.40
II. 48.95	17.73	32.24	trace	0.60	99.57

corresponding with A<sub>2</sub>B<sub>14</sub> and A<sub>1</sub>B<sub>3</sub>, whilst for the mineral from Hokuto the composition ranges from A<sub>1</sub>B<sub>3</sub> to A<sub>8</sub>B<sub>5</sub> (where A = anglesite, B = barytes). The optical characters are intermediate between those of anglesite and barytes, and this supports the suggestion that the mineral is an isomorphous mixture. The barytes, whether containing lead or not, is radioactive, ranging from 0.32 to 1.37 × 10<sup>-10</sup> curie units per grain of mineral. It also exhibits a self-luminous effect, and when heated glows brilliantly (thermoluminescence). L. J. S.

**Analyses of Dolomites.** C. L. HARDING, J. B. SHUMAKER, and A. W. ROTHROCK (*Chem. News*, 1920, **121**, 50—52).—Twenty analyses are given of specimens (crystals and rocks) labelled as dolomite; some proved to be ordinary limestone or calcite, and in one case a sandstone (compare this vol., ii, 118). L. J. S.

**Lead Minerals from the Wreck of a Fire-ship.** ARTHUR RUSSELL (*Min. Mag.*, 1920, **19**, 64—68).—Cavernous masses of metallic lead mixed with charcoal were taken up in 1846 from beneath the partly fused lead pump of a fire-ship which was wrecked in Falmouth Harbour in the year 1780. They show small crystals of cotunnite (PbCl<sub>2</sub>), anglesite (PbSO<sub>4</sub>), leadillite (4PbO<sub>2</sub>SO<sub>3</sub>·2CO<sub>2</sub>·H<sub>2</sub>O), and galena (PbS). These were evidently formed by the action of sea-water on the lead. L. J. S.

**Nephelite from Parco Chigi, Ariccia, Rome.** FRANCESCO STELLA STARRABBA (*Riv. Min. Crist. Ital.*, 1917, **48**, 52—64).—Material eminently suitable for analysis was supplied by clear, colourless crystals from a volcanic bomb consisting mainly of biotite. The refractive indices,  $\omega = 1.5417$ ,  $\epsilon_{\infty} = 1.5382$ , etc., are at the higher limit for nephelite. D<sup>25</sup> 2.65.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Cl	SO <sub>3</sub>	H <sub>2</sub> O	Total
42.57	33.58	0.68	2.15	0.06	14.48	5.73	trace	0.29	0.15	99.69

This gives the ratios  $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{RO}=2:12:1:1:01$ . Deducting  $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$  and  $(\text{Ca},\text{Mg})\text{Al}_2\text{Si}_2\text{O}_8$ , and plotting the remaining  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$  on a triangular diagram, all recent analyses of nephelite fall on a line between the limits  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$  and  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_{10}$ , the present analysis being nearest to the latter. The differences in composition of nephelite are explained by mixtures of these four molecules, but which of them exerts an influence on the variations in refractive indices could not be determined.

L. J. S.

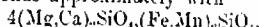
**So-called Hydrocastorite from Elba.** PROBO COMUCCI (*Atti R. Accad. Lincei*, 1920, [v], 29, i, 264-267).—Doubts have been cast by Manasse (A., 1902, ii, 90) and D'Achiardi (A., 1906, ii, 555) on Grattarola's view that hydrocastorite represents a definite mineral species (A., 1878, 119). The author's analysis of Grattarola's mineral gives the percentage composition:

$\text{H}_2\text{O}$ .	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{Na}_2\text{O} + \text{K}_2\text{O}$ (by difference).
16.60	56.63	18.73	0.42	5.56	2.04

From these results and from the physical properties of the mineral the author draws the conclusion that it represents, not a definite mineral, but either a mixture of certain secondary minerals of uncertain and varying composition or, sometimes, simply somewhat impure stilbite.

T. H. P.

**Olivine from Etna.** FRANCESCO SIELLA STARRABBA (*Mem. Classe Sci. R. Accad. Zelanti, Acireale*, 1917, [iii], 9, 41-65).—Small crystals occurring in tuffs are separated according to colour and crystal-habit into: I, olivine of a clear green colour and fairly transparent,  $D\ 3.42$ ,  $\gamma\ 1.707$ ; II, hyalosideritic olivine of a dark brownish-green colour and almost transparent,  $D\ 3.55$ ,  $\gamma_{\text{ns}}\ 1.7303$ . Analysis I corresponds approximately with



and II with  $7(\text{Mg},\text{Ca})_2\text{SiO}_43(\text{Fe},\text{Mn})_2\text{SiO}_4$ . The frequent presence of ferric oxide in volcanic olivine is commented on.

$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{Cr}_2\text{O}_3$ .	$\text{FeO}$ .
I. 37.97	0.05	1.01	5.24	—	14.26
II. 37.43	0.57	0.71	5.82	trace	19.34
( $\text{Co},\text{Ni}$ ) $\text{O}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ ?	Total.
I. —	0.32	0.54	40.71	0.34	100.44
II. 0.11	0.64	1.00	34.43	0.14	100.19

L. J. S.

**"Titanolivine" from the Ala Valley, Piedmont.** F. ZAMBONINI (*Bull. Soc. franç. Min.*, 1919, 42, 250-279).—"Titanolivine" is of frequent occurrence in the serpentine rocks of the Alps, and its presence accounts for the wide diffusion of titanium in these rocks. Dark reddish-brown crystals found at several places in the Ala valley agree in their crystallographic

constants ( $a : b : c = 1.0735 : 1.5.667$ ,  $\beta = 89^{\circ}59\frac{1}{2}'$ ) and optical orientation with clinohumite, but they differ chemically from this in containing some titanium and also hydroxyl in place of fluorine. Analysis gave:

$\text{SiO}_2$	$\text{TiO}_2$	$\text{PbO}$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{GIO}$	$\text{FeO}$	$\text{MnO}$	$\text{NiO}$	$\text{MgO}$
36.83	1.92	0.14	0.42	0.07	1.30	4.90	0.28	0.07	51.53
					$\text{H}_2\text{O}$	$\text{H}_2\text{O}$			
$\text{CaO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$			( $<110^\circ$ )	( $>110^\circ$ )	$\text{F}$		Total
0.03	0.09	0.03			0.05	2.99	0.03		100.68

corresponding with the ratios  $\text{SiO}_2 : \text{TiO}_2 : \text{RO} : \text{H}_2\text{O} (+ \text{F}) = 1 : 2.23 : 0.26$ , and with the formula  $4\text{Mg}_2\text{SiO}_4\text{Mg}(\text{OH})_2$ . The mineral is decomposed by hydrochloric acid. Water is expelled only at a high temperature. Glucinum has been previously detected in a mineral of this group by Jannasch and Locke (A., 1894, ii, 459), but lead is unusual. The earlier analyses of "titanolivine" by A. Damour (1855 and 1879) and G. Auelli (A., 1905, ii, 176) agree with the clinohumite formula only when it is assumed that titanium replaces magnesium, and they are probably at fault. The name "titanolivine" being thus inadmissible for this mineral, *titanhydroclinohumite* is suggested as an alternative. L. J. S.

### Analytical Chemistry.

**Method of Stating Analytical Results.** A. THIEL (*Chem. Zeit.*, 1920, **44**, 525-526. Compare this vol., ii, 187).—The author suggests a nomenclature for equivalent or molecular quantities, for example, "norm" (symbol  $gN$ ) for gram-equivalent, "mol" ( $gM$ ) for gram-molecule, etc. W. P. S.

**The Significance of the "Specific Refraction" for Analytical Chemistry.** N. SCHOONL (*Rec. trav. chim.*, 1920, **39**, 594-599).—The specific refraction,  $(n-1)/d$ , may serve as a confirmatory measurement for the identification of an unknown organic compound, but its application is somewhat limited. W. G.

**Flurometry. Quantitative Analysis by Comparative Fluorescence.** L. J. DESHA (*J. Amer. Chem. Soc.*, 1920, **42**, 1350-1363).—A new method of microanalysis is described, of the same order of sensitiveness as colorimetry and nephelometry, which should prove generally applicable to the estimation of minute quantities of the considerable number of substances which are either fluorescent themselves or may be rendered so by the addition of a suitable reagent. Ultraviolet rays from a quartz mercury

lamp are filtered from most of the visible radiation and used to excite fluorescence in solutions of such substances contained in the comparison cylinders of the Kober nephelometer. The intensity of the fluorescent light thus produced, as observed in the eyepiece of the instrument, is equalised in the usual manner by altering the heights of the exposed columns. For sufficiently dilute solutions, the curves obtained by plotting the scale readings against concentrations are quite regular. These calibration curves are drawn for solutions containing 0.5-2 mg. per litre of quinine sulphate in *N*-sulphuric acid, and for solutions of 2-4 mg. per litre of aniline iodoesin in *N*/10-alkali. Such a curve differs from that of inverse proportionality (the colorimetric curve) much more than from one drawn according to the nephelometric formula. Some peculiarities of the latter are indicated, and it is shown that when two constants are used (one for solutions stronger than the standard and the other for those more dilute), the values corresponding with the fluoreinetric readings may be taken from the nephelometric curve with an average error of 1%. J. F. S.

**A Gas Analysis Apparatus Accurate to 0.001% mainly designed for Respiratory Exchange Work.** AUGUST KROGH (*Biochem. J.*, 1920, **14**, 267-281).—The apparatus contains two improvements on the usual arrangements. The more important of these is the use of three separate gas burettes, the first being used exclusively for moving the air to and from the absorption pipettes, the second being of a size suitable for measuring the air before and after the absorption of carbon dioxide, and the third is for measuring the air after the absorption of oxygen. The water vapour necessary for saturating the sample of air, after it comes from the absorption pipettes, is supplied by the first burette. The other two burettes contain just enough water to ensure that the samples remain saturated.

The second improvement is that the mercury is raised and lowered in the burettes, not by raising and lowering a mercury reservoir, but by means of air pressure. This obviates the use of rubber connexions between the burettes and the reservoirs, and also considerably facilitates the analytical manipulations.

The apparatus is fully sketched in the original, and detailed instructions are given for conducting an analysis. W. G.

**Titration with the Hydrogen Electrode.** W. D. TREADWELL and L. WEISS (*Helv. Chim. Acta*, 1920, **3**, 433-446).—The authors describe a hydrogen electrode which, when in steady use, retains its activity for six weeks, and is then easily regenerated. The change in potential of the electrode during acidimetric titrations may be measured with sufficient accuracy by means of a millivoltmeter, and it may be used for the titration of both strong and weak acids. With the latter, the equilibrium constants may be calculated very simply from the fall in potential during the

titration. Strong acids in presence of weak acids may also be estimated.

T. H. P.

**Standardisation of Sodium Thiosulphate, Arsenious Acid, Potassium Bromate, Potassium Iodate, etc., Solutions, by means of Standard Sulphuric Acid Solution.** L. BERTIAUX (*Ann. Chim. anal.*, 1920, [ii], 2, 207-208).—The equivalent quantity of iodine liberated from a mixture of potassium iodate and potassium iodide by a definite volume of standard sulphuric acid solution is used for the standardisation of thiosulphate and arsenious acid solutions. Variations of the reaction are employed for the standardisation of the other solutions mentioned.

W. P. S.

**Indicators used for Estimating Free Acid in Pickling Solutions.** C. L. BOYLE (*J. Ind. Eng. Chem.*, 1920, 12, 571-572).—Sodium or potassium thiocyanate solution is recommended as the indicator, since the end-point shown by ordinary indicators is obscured by the large amount of ferrous sulphate present in the pickling solution.

W. P. S.

**The Incineration of Organic Substances Prior to Analysis for the Mineral Elements which they Contain. Application to the Analysis of Blood.** A. DESGRÉZ and J. MEUNIER (*Compt. rend.*, 1920, 171, 179-182).—For the incineration of organic substances for subsequent ash analysis, the authors recommend that the material should first be thoroughly dried, and then ignited and allowed to burn at as low a temperature as possible. In this way, a carbonised material is obtained which, when further incinerated, readily becomes incandescent and leaves a white ash. If excess of alkali salts is present, these should be extracted with water before the final incineration. This method has been applied to the ash analysis of blood, and the presence of copper, manganese, and lithium detected.

W. G.

**Volumetric Estimation of Sulphuric Ions.** JOSEPH ERLICH (*Ann. Chim. anal.*, 1920, [ii], 2, 214-215).—The solution, containing about 0.01 gram of sulphuric acid as alkali salt, is neutralised, boiled with the addition of barium carbonate, set aside for twelve hours, filtered, the precipitate washed, and the alkalinity of the filtrate titrated with *N*:10-acid. The alkalinity is equivalent to the sulphuric ions present originally.

W. P. S.

**Estimation of Nitrate Nitrogen in Nitrates and Fertilisers.** H. C. MOORE (*J. Ind. Eng. Chem.*, 1920, 12, 669-673).—From 0.8 to 1.7 gram of the sample, according to the quantity of nitrate present, is mixed with 35 c.c. of sulphuric acid containing 1 gram of salicylic acid, the mixture is shaken for fifteen minutes, 5 grains of sodium thiosulphate are added, and the mixture heated until frothing ceases. Five grams of potassium sulphate and 0.5 gram

of mercury are then added, and the heating is continued for ninety minutes after a clear solution has been obtained. Sodium sulphide is added in the subsequent distillation of the ammonia.

W. P. S.

**Preparation of Diphenylamine-sulphuric Acid.** FR. HAUN (*Zeitsch. Nahr. Genussm.*, 1920, **39**, 355—356).—The sulphuric acid used in preparing diphenylamine reagent for the detection of nitrates should be free from nitric acid, as shown by the brucine test. Sometimes the reagent made with sulphuric acid free from nitric acid becomes blue in colour after a short time; this is due to the presence of ferric salts in the sulphuric acid. Such acid may still be used if it is heated previously to boiling and then cooled; the ferric salts are reduced permanently by this treatment, and the acid does not give a blue coloration when mixed with diphenylamine. The course of the reduction may be followed by adding a trace of permanganate before heating the acid. The permanganate is also reduced, and the presence of the manganese tends to increase the sensitiveness of the reagent. W. P. S.

**Iodic Acid as a Characteristic Microchemical Reagent for Gaseous Ammonia.** GEORGES DENISIS (*Compt. rend.*, 1920, **171**, 177—179).—When one drop of a 10% aqueous solution of iodic acid is exposed to an atmosphere containing ammonia, it immediately becomes covered with a crystalline film. These crystals may readily be identified under the microscope as flattened, quadratic crystals of the normal iodate,  $\text{NH}_4\text{IO}_3$ . None of the volatile amines examined gave this reaction under these conditions. For the detection of traces of ammonium salts in a solution, the latter is first concentrated by evaporation, and then the ammonia is liberated by the action of magnesium oxide and tested as above.

W. G.

**The Technique of the Estimation of Phosphoric Acid as Barium Phosphomolybdate.** S. POSTERNAK (*Bull. Soc. chim.*, 1920, [iv], **27**, 564—568).—Very full details are given for preparing the solutions for, and conducting an estimation by, the method already described (this vol., ii, 505). W. G.

**Estimation of Solvent Carbon Dioxide in Water.** H. NOLL (*Zeitsch. angew. Chem.*, 1920, **33**, i, 182—184).—It was shown by Tillmans and Heublein (*A.*, 1913, ii, 51) that free carbon dioxide in soft water has a much greater solvent action on calcium carbonate than the same amount of carbon dioxide in hard water, since that portion required to keep calcium hydrogen carbonate, etc., in solution has no solvent action on calcium carbonate. Curves plotted by Tillmans and Heublein enable the amount of solvent carbon dioxide to be read directly when the amounts of free and combined carbon dioxide are known. In the case of waters containing iron hydrogen carbonate, the semi-combined and the combined

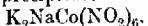
carbon dioxide in the iron compound are titrated simultaneously with the free carbon dioxide, and, as a correction, 1·1 mg. of carbon dioxide must be deducted for each mg. of ferric oxide present. For this reason, the filtrate from plants used for removing iron from water will often yield higher values for free carbon dioxide than the original water. The combined carbon dioxide in water may be estimated by titration with hydrochloric acid, with methyl-orange as indicator, and also by boiling the water with excess of acid and titrating the excess, with phenolphthalein as indicator. The carbon dioxide in combination with iron is estimated by the first method, but not by the second. The results for solvent carbon dioxide in waters free from iron are most trustworthy when, in addition to calcium hydrogen carbonate, the water also contains considerable quantities of the hydrogen carbonates of magnesium and sodium. The solvent action of free carbon dioxide is probably reduced to the greatest extent by iron hydrogen carbonate, and successively less by the hydrogen carbonates of calcium, magnesium, and sodium.

C. A. M.

**Hæmato-respiratory Functions. II. The Henderson-Morriss Method for Determining the Carbon Dioxide in Plasma and in Whole Blood.** HOWARD W. HAGGARD (*J. Biol. Chem.*, 1920, **42**, 237—244).—A careful study of the Henderson-Morriss method (A., 1917, ii, 506) of determining the carbon dioxide of plasma or whole blood, and a comparison with the méthode of Van Slyke and Cullen (A., 1917, i, 521), show that the various corrections almost exactly neutralise each other. At ordinary temperatures and barometric pressures, the reading on the gas burette for the carbon dioxide absorbed during the gas analysis (corrected only for the carbonate of the ammonia solution) may be taken as indicating directly, within the error of the method, the amount of carbon dioxide contained in the blood or plasma. With this method, the analysis of whole blood is as easy as that of plasma.

W. G.

**Estimation of Potassium and its Separation from Sodium by means of Sodium Cobaltinitrite.** P. WENGER and C. HÄMEN (*Ann. Chim. anal.*, 1920, [ii], **2**, 198—199).—The potassium sodium cobaltinitrite precipitate, obtained in the usual way, is dissolved in hydrochloric acid, and the cobalt then estimated electrolytically or gravimetrically. The precipitate has the composition



and the potassium may be calculated from the weight of cobalt found.

W. P. S.

**Titration of Ammonium Hydrogen Fluoride.** WALLACE S. CHASE (*J. Ind. Eng. Chem.*, 1920, **12**, 567—568).—Methyl-orange, litmus, lacmoid, methyl-red, and cochineal are untrustworthy as indicators in the presence of free hydrofluoric acid, and ammonia interferes with the sensitiveness of phenolphthalein. If,

however, the ammonium hydrogen fluoride solution is treated with an excess of calcium chloride, the hydrochloric acid liberated may be titrated, using methyl-orange as indicator. There is no need to remove the precipitated calcium fluoride by filtration.

W. P. S.

**Estimation of Calcium by Different Methods.** GEORGE E. EWE (*Chem. News*, 1920, **121**, 53-56).—The following average results were obtained in the estimation of calcium in a sample of calcite by different methods: (1) precipitation as calcium oxalate and weighing as calcium carbonate, 99.57%; (2) precipitation as calcium carbonate and weighing as such, 100.07%; (3) liberation of carbon dioxide with hydrochloric acid and weighing the carbon dioxide in potassium hydroxide solution, 100.03%; (4) precipitation as calcium oxalate and weighing as calcium oxide, 99.86%; (5) precipitation as calcium sulphate and weighing as such, 99.68%; (6) precipitation as calcium oxalate and weighing as calcium sulphate, 100.39%; (7) precipitation as calcium oxalate and titration with potassium permanganate, 99.68%; (8) precipitation as oxalate from a slightly acid solution, 99.87%; (9) liberation of carbon dioxide and calculation of loss into  $\text{CaCO}_3$ , 99.80%; (10) residual titration method, 99.75%. The theoretical amount of calcium (as  $\text{CaCO}_3$ ) in the material was 99.959%. C. A. M.

**Acidity and Acidimetry of Soils. III. Comparison of Methods for Estimating Lime Requirements of Soils with Hydrogen Electrode. IV. Proposed Method for Estimation of Lime Requirements of Soils.** HENRY G. KNIGHT (*J. Ind. Eng. Chem.*, 1920, **12**, 559-562).—The vacuum method (A., 1916, i, 459) appears to be the most trustworthy for estimating the lime requirement of soils, and the hydrogen electrode method (this vol., i, 587) yields results which agree with those given by the vacuum method, provided that the soil is shaken with lime for more than three hours before the hydrogen-ion concentration is determined. The Hopkins (A., 1916, i, 459) and hydrogen electrode methods are the best for measuring the reduction of acidity in limed soils. A method proposed for estimating the lime requirements of soils consists in boiling a mixture of 10 grams of the soil, 25 c.c. of normal potassium chloride or sodium chloride solution, and an excess of calcium carbonate for ten minutes, and measuring the volume of the carbon dioxide evolved. The results obtained agree with those found by the hydrogen electrode method. W. P. S.

**Rapid Identification of the Two Ionic Elements of Barium Sulphate.** G. DEMICÉ (*Bull. Soc. chim.*, 1920, [iv], **27**, 560-564).—A more detailed account of work already published (compare this vol., ii, 398). W. G.

**Estimation of Lead in Chemicals in Acid Solution.** NORMAN EVERE (Pharm. J., 1920, **105**, 85-86).—In the colorimetric (sulphide) estimation of lead in acid solution, the test

solution and the comparison solution should have the same hydrogen-ion concentration, otherwise the colorations obtained are not comparable. The author recommends that the acidity should be neutralised before the sulphide is added, and that bromo-phenol-blue (tetrabromophenolsulphonphthalein) should be used as the indicator; this indicator is colourless at the neutral point. Iron does not interfere under these conditions, and the effect of copper may be prevented by the addition of cyanide. If both iron and copper are present, the copper should be separated by adding alum solution and ammonia, collecting the aluminium hydroxide (this precipitate also contains the lead), dissolving it in acid, and treating this solution as described, but without the addition of cyanide.

W. P. S.

**Estimation of Mercury in Organic Combination by means of Zinc Filings.** MAURICE FRANCOIS (*Bull. Soc. chim.*, 1920, [iv], 27, 568).—A simplification of the method previously described (this vol., ii, 269), which avoids the necessity for heating. About half a gram of the dry, powdered organic matter is weighed into a tared, conical flask. To it is added 30 c.c. of ether, 10 c.c. of alcohol, 1 c.c. of concentrated hydrochloric acid, and, immediately, 1 gram of zinc turnings. The mixture is shaken once and left for half an hour. Another gram of zinc is added, the mixture shaken, and again left for half an hour, when a third gram of zinc is added, and the mixture left twenty-four hours. By this time all the mercury is deposited on the zinc, and the estimation is continued as described (*loc. cit.*). W. G.

**Modification of Caron and Raquet's Reaction for Manganese.** G. DENIGES (*Ann. Chim. anal.*, 1920, [ii], 2, 215—216).—This reaction (A., 1919, ii, 351, 438) may be simplified as follows: 5 c.c. of the manganese solution and a few drops of sodium hydroxide solution are shaken thoroughly in a testtube until a brown coloration is obtained: saturated oxalic acid solution is then added drop by drop. The brown coloration disappears and the characteristic red coloration develops. W. P. S.

**The Use of Phenolphthalein and Diphenylamine in the Method with Persulphate for the Estimation of Manganese.** D. H. WESTER (*Rec. trav. chim.*, 1920, **39**, 600—602). Compare this vol., ii, 451).—The author finds that the use of an alkaline solution of phenolphthalein as a comparison solution, and of diphenylamine for deepening the colour, in the estimation of manganese colorimetrically, as recommended by Tillmans and Mildner (A., 1915, ii, 583), does not give exact results. W. G.

**Estimation of Manganese in Biological Material together with Data on the Manganese Content of Human Blood and Tissues.** CLARENCE K. REIMAN and ANNIE S. MINOT (*J. Biol. Chem.*, 1920, **42**, 329—345).—For the preliminary preparation

the tissue or blood, by means of which any manganese present is converted into the sulphate, the authors recommend either a modification of Bertrand's method (compare A., 1912, ii, 459, 662), the fusion with potassium acid sulphate being carried out at 500—600° in quartz vessels, or the digestion with sulphuric, nitric, and hydrochloric acids in pyrex Kjeldahl flasks. It is noted that quartz vessels are liable to contain manganese, and must be tested by a preliminary fusion. For the conversion of the manganese sulphate into permanganate, the authors further slightly modify Bertrand's modification (*loc. cit.*) of Marshall's method (compare *Chem. News*, 1901, **83**, 76) with potassium persulphate.

A series of results is given for the manganese content of human blood, the values obtained varying from 0.004 to 0.02 mg. per 100 grams, most of the cases coming between the limits 0.01 and 0.02 mg. No abnormality in manganese content was shown by the few pathological cases examined, except, perhaps, in the case of syphilis of long duration, where the manganese is low.

The results for the manganese contents of human organs from fourteen autopsies are given, manganese being invariably present. The liver has the highest manganese content, 0.17 mg. per 100 grams of wet tissue on the average.

W. G.

#### Estimation of Small Quantities of Iron as Thiocyanate.

RICHARD WILLSTÄTTER (*Ber.*, 1920, **53**, [B], 1152—1154).—Small amounts of iron, such as are found in peroxidase preparations, can be estimated rapidly and accurately in the following manner. The solution under investigation (0.5—1 c.c.) is treated with concentrated hydrochloric acid (0.5 c.c.) and made up to 50 c.c. with freshly prepared ammonium thiocyanate solution (40%, or, with larger quantities of iron, 10%). The coloration is matched by the use of standard solutions of iron, which are similarly treated. Difficulties are caused by the presence of iron in the purest commercial ammonium thiocyanate and by the instability of ferric thiocyanate in solution; the latter effect is due to the gradual reduction of the ferric salt by the thiocyanate, but the process does not appear to be catalysed by the ferrous salt formed. The difficulty first named is overcome by boiling the ammonium thiocyanate solution for a short time, after which it remains colourless when cooled.

H. W.

**Use of Potassium Xanthate for the Detection and Separation of Cobalt in the Presence of Nickel.** LOUIS COMPIN (*Bull. Soc. Pharmacol.*, 1920; from *Ann. Chim. anal.*, 1920, [ii], 2, 218—220).—When a solution containing nickel and cobalt is acidified with hydrochloric acid and treated with a slight excess of potassium xanthate, the two metals are precipitated as xanthates. On the addition of ammonia, the nickel compound dissolves to give a blue solution, whilst the cobalt compound remains insoluble. When this method is used for the estimation of cobalt in nickel,

the ammoniacal solution of the cobalt compound should be acidified with hydrochloric acid, and the precipitation repeated in order to recover a trace of cobalt which dissolves in the ammonia.

W. P. S.

**Estimation of Zirconium and Titanium in Zirconium Ores.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1920, **42**, 1439—1448).—A method of estimating zirconium, titanium, and the total rare earths in zirconium ores, is described. The method is found to be applicable in the presence of any or all of the elements which have ever been found in zirconium ores.

Four grams of borax are fused and allowed to solidify in a platinum crucible, 0.3 gram of finely powdered ore (100 mesh) added, and the mixture heated over a Meker burner and stirred with a platinum rod for thirty minutes. The cooled mass is placed in hydrochloric acid (1:5) in a beaker and warmed on a steam-bath. The solution is transferred to a platinum dish, treated with sulphuric acid (1:20), and evaporated until fumes of acid are evolved. The concentrated liquid is cooled, diluted to 100 c.c., and the impure silica filtered off and washed, and the washings added to the filtrate. The filtrate is warmed overnight to precipitate small amounts of phosphorus as zirconium phosphate. The precipitate is filtered and washed with 5% ammonium nitrate, and the washings added to the filtrate. Ammonium chloride (5 grams) is added to the filtrate, followed by an excess of ammonia, and the solution boiled for a few minutes, filtered, and the precipitate washed with 2% ammonium nitrate, and the filtrate discarded. The precipitate is dissolved in hot 5% sulphuric acid and the paper thoroughly washed (solution A). The filter paper, together with the filter papers containing the silica and the zirconium phosphate, is ignited in the original crucible, the ash moistened and treated with 1 c.c. of sulphuric acid and 5 c.c. of hydrofluoric acid, and ignited until all the sulphuric acid is expelled. The residue is ignited with a small amount of sodium carbonate. The fused mass is digested with water and filtered. The residue is well washed with hot water, ignited, and fused with sodium hydrogen sulphate; the cooled fusion is dissolved in 5% sulphuric acid, and the solution added to the solution A. The foregoing treatment removes phosphoric acid and recovers any zirconium which was present in the silica. The solution containing the whole of the metals is neutralised until it contains about 1% (by volume) of free sulphuric acid, treated with hydrogen sulphide, and filtered if necessary. The filtrate is made up to 200 c.c., treated with tartaric acid in amount equal to five times the weight of the base in solution, made ammoniacal, and saturated with hydrogen sulphide, and any sulphide filtered off. The acidity of the solution is brought to 10% of sulphuric acid in a volume of 400 c.c., the solution boiled to expel hydrogen sulphide, and cooled to 4—15°. An excess of a cold 6% aqueous solution of cupferron is added. An excess is indicated by a fine, white precipitate, which

redissolves, instead of a curdy one, which remains. After digesting for five minutes, the precipitate is filtered with gentle suction, washed with 10% (by volume) hydrochloric acid, and dried. The paper and precipitate are ignited in a weighed platinum crucible over a blowpipe flame, and weighed. The weight is that of the oxides of zirconium, titanium, and the rare earth metals. After weighing, the oxides are fused with potassium hydrogen sulphate, taken up with 10% (by volume) sulphuric acid, and diluted to exactly 100 c.c. This is divided into two 50 c.c. portions, and the titanium estimated in one and the rare earths in the second, and the zirconium obtained by difference. *Estimation of titanium.*—If the content of titanium is low, it is estimated by Weller's colorimetric method, whilst if it is high, it is reduced to the sesquioxide in a Jones' reductor containing ferric alum and phosphoric acid in the receiver, and then oxidised to the dioxide by titration with potassium permanganate. *Estimation of the rare earths.*—The hydroxides are precipitated with excess of potassium hydroxide, filtered, washed, and then washed into a platinum dish with 5% hydrofluoric acid. The solution is evaporated nearly to dryness and treated with 5 c.c. of 5% hydrofluoric acid. If no precipitate is present, the rare earths are absent; if present, it is filtered, washed with 5—10 c.c. of the same acid, transferred to a platinum dish, and ignited. Sulphuric acid is then added, and the whole evaporated to dryness, dissolved in dilute hydrochloric acid, and the rare earth hydroxides precipitated with ammonia, filtered, washed, redissolved in hydrochloric acid, and evaporated to dryness. The residue is treated with 5 c.c. of boiling 5% oxalic acid solution, and, after digesting for fifteen minutes, filtered, washed with 20 c.c. of 5% oxalic acid, ignited, and weighed. The accuracy of the method is shown by a series of concordant analyses of diorite to which weighed amounts of zirconium, titanium, thorium, cerium, and phosphate had been added.

J. F. S.

**Estimation of Zirconium in Steel.** G. E. F. LUNDELL and H. B. KNOWLES (*J. Ind. Eng. Chem.*, 1920, **12**, 562—567).—A critical review of methods published previously. The authors also give a method for the estimation of silicon, aluminium, titanium, and zirconium in steels which may contain other elements, such as tungsten, chromium, vanadium, phosphorus, molybdenum, copper, nickel, cobalt, uranium, and cerium. The steel is dissolved in hydrochloric acid with the addition of nitric acid. Silica is separated, the greater part of the iron removed by extraction with ether, the hydrochloric acid solution then treated with excess of sodium hydroxide, and the precipitate collected. This precipitate is dissolved in hydrochloric acid, the solution nearly neutralised, tartaric acid is added, the mixture treated with hydrogen sulphide, then rendered ammoniacal, and filtered. After the filtrate has been acidified with sulphuric acid and boiled to expel hydrogen sulphide, the zirconium and titanium are precipitated together by "cupferron"; the titanium is estimated subsequently, either

colorimetrically or volumetrically, in the mixed oxides. [See, further, *J. Soc. Chem. Ind.*, 1920, September.] W. P. S.

**Immediate Analysis by Fractional Distillation, Method of Maxima and Minima.** CHARLES MOURET, CHARLES DUFFRAISSE, and PAUL ROBIN (*Bull. Soc. chim.*, 1920, [iv], **27**, 523—527).—The method described, which is applicable to the separation of mixtures of substances with boiling points close together, consists of successive fractional distillations, the division into fractions being controlled, not by the boiling points, but by maximum or minimum values of physical properties, such as density, refractive index, viscosity, etc. The rectification is continued, similar fractions being united for further fractionation, until a fraction is obtained which, when subdivided by slow distillation, gives fractions all of which possess identical boiling points and physical properties.

A simple vaselin manometer is described by means of which very slight variations in pressure during distillation may be noted, and it allows of a distillation being interrupted and then very readily resumed at the same reduced pressure. W. G.

**Critical Study of Methods for the Detection of Methyl Alcohol.** ALEXANDER O. GETTLER (*J. Biol. Chem.*, 1920, **42**, 311—328).—Fifty-eight tests for the detection of methyl alcohol were critically studied to ascertain their trustworthiness, specificity, and sensitiveness, and the influence of foreign substances on them. They may be divided into two groups: (1) in which the methyl alcohol is oxidised to formaldehyde, which is then detected; (2) in which direct tests for methyl alcohol itself are applied. As oxidising agents for conversion of the methyl alcohol into formaldehyde, the author prefers alkaline permanganate or potassium dichromate and sulphuric acid. The colorimetric tests for the detection of formaldehyde which he considers most trustworthy are: with (1) phenylhydrazine + ferric chloride + hydrochloric acid (*Meth.*, A., 1906, ii, 589); (2) phenylhydrazine + sodium nitroprusside + sodium hydroxide (*Meth.*, *loc. cit.*); (3) apomorphine sulphate (*Wolff*, A., 1919, ii, 482); (4) peptone + ferric chloride + hydrochloric acid (*Salkowski*, A., 1919, ii, 249); (5) reduced magenta + sulphuric acid (*Denigès*, A., 1910, ii, 357, 461). These colour tests are extremely sensitive, 1 part in 200,000 being easily detected. Two confirmatory tests in which crystalline products are obtained are: (1) with  $\beta$ -naphthol + hydrochloric acid (Mulliken, "A method for the identification of pure organic compounds," 1911); (2) with concentrated ammonia, giving hexamethylenetetramine, which gives characteristic crystals with mercuric chloride (*Romijn*, A., 1896, ii, 280). These two tests require the presence of 5% of methyl alcohol.

All the methods, which are applied directly for methyl alcohol, require a large amount of methyl alcohol. Of the twelve examined, the method of Leach and Lythgoe (A., 1905, ii, 655), in

which the relationship between specific gravity and refractive index is determined, is the most outstanding. As a colorimetric test, that described by Vivario (A., 1914, ii, 780), in which the alcohol is converted into potassium cyanide, is very good.

Details of the typical procedures for the detection of methyl alcohol in liquors and in tissues are given, and there is a full bibliography.

W. G.

**Diazometric Estimation of Phenol and of certain of its Homologues.** ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1920, 12, 568-570).—The method depends on the coupling of phenols with diazonium salts to form insoluble hydroxyazo-compounds. The reagent is prepared by mixing equal volumes of *N*/10-*p*-nitro-aniline solution and 1% sodium nitrite solution, and is standardised against *β*-naphthol. The phenol solution to be titrated is treated with 10% sodium acetate solution and basic lead acetate solution, and the reagent is added with constant stirring. Small, filtered portions of the mixture are tested from time to time with a drop of the reagent or a drop of phenol solution in order to ascertain the progress of the titration. [See, further, *J. Soc. Chem. Ind.*, 1920, September.]

W. P. S.

**Analysis of Phenolsulphonic Acids.** LOUIS DESVERGNES (*Ann. Chim. anal.*, 1920, [ii], 2, 211-214).—About 5 grams of the sample are dissolved in water and diluted to 200 c.c. Ten c.c. of the solution are boiled for fifteen minutes with hydrochloric acid and bromine, diluted to 200 c.c., cooled, filtered, and the sulphuric acid is estimated in the filtrate as barium sulphate; this gives the total sulphuric acid ( $H_2SO_4$ ) present. Ten c.c. of the solution are then titrated with *N*/2-sodium hydroxide solution, using methyl-orange as indicator; the combined sulphuric acid is calculated from the formula  $(T-S)/2$ , where  $T$  is the total sulphuric acid and  $S$  the sum of the total sulphuric acid and one-half of the combined sulphuric acid. The phenol is estimated by treating 10 c.c. of the solution with 100 c.c. of water and 50 c.c. of hydrochloric acid, adding a definite quantity of standardised potassium bromide-bromate solution, heating the mixture at 50° for thirty minutes in a closed vessel, and then titrating (iodometrically) the excess of bromine. Calculation gives the amount of free sulphuric acid present, and the proportion of phenol to combined sulphuric acid indicates the amounts of mono- and di-sulphonic acids in the sample.

W. P. S.

**Use of Potassium Ferrocyanide in the Analysis of Sugars by Alkaline Copper Solutions.** E. CORDONNIER (*Bull. Sci. pharmacol.*, 1920, 27, 137-138).—The use of potassium ferrocyanide, in the amounts indicated by its advocates, is capable of causing a complete reduction of Fehling's solution if the boiling is sufficiently prolonged. The method of Causse-Bonnans leads to

very serious errors if the conditions of heating are not accurately controlled.

## CHEMICAL ABSTRACTS.

**Blood Sugar Concentration and Blood Sugar Methods.** H. F. Höst and ROLF HATLEHOL (*J. Biol. Chem.*, 1920, **42**, 347—358).—Bang and Hattelhol's method (compare A., 1918, ii, 279), and Hagedorn and Jensen's method (compare *Ugesk. Læger*, 1918, **80**, 1217), give in normal individuals and in diabetics values for the blood sugar concentration which agree approximately. The method of Folin and Wu (A., 1919, ii, 308), and particularly the modification by Myers and Bailey (A., 1916, i, 300) of Benedict's method, may, in the case of diabetics with hyperglycemia, give results which are too high. W. G.

**Method for the Estimation of Acetic Acid in Acetates.** OSCAR A. PICKETT (*J. Ind. Eng. Chem.*, 1920, **12**, 570—571).—Xylene is used in place of water as a carrier for the acetic acid in the distillation of the acetate with phosphoric acid. About 350 c.c. of xylene are used for 2.5 grams of the acetate, and the distillation is continued until only a thin film of xylene remains on the surface of the phosphoric acid solution in the distillation flask. W. P. S.

**Degree of Alkalinity Necessary for the Phloroglucinol Test for Formaldehyde.** PAUL J. HANZLIK (*J. Biol. Chem.*, 1920, **42**, 411—413).—The degree of alkalinity necessary for a minimum positive reaction in the phloroglucinol test for formaldehyde is  $P_n = 12.13$ , or the equivalent of the alkalinity of 0.01*N*-sodium hydroxide. For an optimum reaction, the alkalinity should be  $P_n = 13.0$ , or 0.1*N*. W. G.

**Estimation of Acetaldehyde in Paracetaldehyde.** W. STÜWE (*Apoth. Zeit.*, 1920, **35**, 153—154; from *Chem. Zentr.*, 1920, iv, 155).—Paracetaldehyde (5 c.c.) is brought into a 100 c.c. flask and frequently shaken during a quarter of an hour with *N*/10-mercuric chloride solution (10 c.c.), potassium iodide free from iodate (2 grams), sodium hydroxide solution (15%, 20 grams), and water (50 grams). The mixture is diluted to 100 c.c. and filtered. Fifty c.c. of the filtrate are treated with gum arabic (0.5 gram), sodium hydroxide solution (5 c.c.), and formaldehyde (3 c.c.); after two minutes, the solution is acidified with dilute acetic acid (15 c.c.), and subsequently cooled. The precipitated mercury is dissolved by addition of a measured volume of *N*/10-iodine solution, and excess of the latter is titrated. H. W.

**Rapid Volumetric Methods for the Estimation of Amino-acids, Organic Acids, and Organic Bases.** FREDERICK WILLIAM FOREMAN (*Biochem. J.*, 1920, **14**, 451—473).—Ammonia, primary, secondary, and tertiary amines, and basic methylene derivatives of secondary amines do not form ionisable compounds with phenolphthalein in aqueous-alcoholic solutions providing the concentration of alcohol is above 80%. In such solutions, therefore,

the acid radicles of the salts of these bases can be titrated accurately with  $N/10$ -potassium hydroxide, using phenolphthalein as indicator. Similarly, when aqueous-alcoholic solutions of certain amino-acids containing about 85% of alcohol are titrated with  $N/10$ -alcoholic potassium hydroxide, the amino- or imino-groups, liberated from their "internal salt" combinations, show no basicity to phenolphthalein, and the carboxyl groups are accurately estimated. Certain amino-acids, however, more particularly dibasic amino-acids and proline, give low results when titrated in alcohol under these conditions, possibly owing to loose combination of alcohol with a carboxyl group, or loose condensation, but a subsequent addition of formaldehyde or acetone results in a disturbance of the equilibrium, and then the carboxyl groups can be titrated quantitatively.

The guanidine nucleus of arginine behaves differently from other nitrogenous bases or basic groups in that it acts as a univalent base in both alcohol and water. Thus it is neutral to phenolphthalein in 85% alcohol solution, the carboxyl group and the guanidine nucleus exactly neutralising each other.

The complete estimation is carried out as follows: (1) Five c.c. of the aqueous solution are titrated with  $N/10$ -aqueous sodium hydroxide. (2) Ten volumes of 97% alcohol are added to 5 c.c. of the aqueous solution, and the mixture is titrated with  $N/10$ -alcoholic potassium hydroxide. (3) To the liquid from titration (2), 12.5 c.c. of neutral 13% aqueous formaldehyde solution are added for every 50 c.c. of alcohol present, and the titration continued to the same end-point. Titration (1) gives useful information when dibasic amino-acids, arginine, and salts of amino-acids are present. Titration (2) gives the correct estimation of a number of amino-acids. In titration (3), the carboxyl groups of all the amino-acids in an amino-acid mixture, except that of arginine, are estimated.

This new volumetric process forms a rapid and accurate method for use in the investigation of many important biochemical problems. For the estimation of volatile bases and amino-acids in "alcoholic extracts" (compare Foreman and Graham-Smith, *J. Hygiene*, 1917, **16**, 144), to an aliquot part of the extract the amount of alcoholic alkali necessary for neutralisation, as determined by titration (3), is added, and the mixture is distilled with steam free from carbon dioxide for about five minutes, the distillate being collected in standard acid. The excess of acid is titrated, using alizarin as indicator, and thus a measure of the volatile bases is obtained. The residual liquid in the distillation flask is free from alcohol, and, owing to the hydrolysis of the alkali salts of the amino-acids, is alkaline. It is titrated with  $N/10$ -acid, and thus a value is obtained for the amino-acids present in the original "alcoholic extract."

W. G.

**Micro-estimation of Urea in Blood by means of Urease.**  
R. BAHLMANN (*Ned. Tijdsch. Geneesk.*, 1920, **64**, [i], 473-478; from *Chem. Zentr.*, 1920, **iv**, 3-4).—The method of Cohen,

Fervaert, and Van Lier is modified in such a manner that the estimation can be made with 0·4 c.c. of blood. The ammonia, obtained by the action of the urease of the soja bean on the urea of the blood in faintly acid solution, is, after addition of alkali, drawn by a stream of air into very dilute hydrochloric acid, and excess of the latter is estimated iodometrically according to Bang's method. A blank experiment is performed with an equal quantity of blood without addition of urease. The amount of urea is calculated from the difference in the titrations in the two experiments.

H. W.

**Estimation of Hydrocyanic Acid in Beans.** A. CZAPSKI (*Zeitsch. anal. Chem.*, 1920, **59**, 80).—Paraffin wax should not be used to prevent frothing of the contents of the distillation flask during the distillation of hydrocyanic acid from cyanogenetic beans; the wax inhibits partly the distillation of the acid, and less than one half of the amount of the latter actually present is found in the distillate.

W. P. S.

**Direct Estimation of Mercury Fulminate in the Mixtures for Detonators.** M. D. MARQUEYROL (*Bull. Soc. chim.*, 1920, [iv], **27**, 448).—The mixture is extracted with a 5% solution of potassium cyanide, and the mercury is estimated by electrolysis in the extract.

W. G.

**A Pyrrole Reaction.** E. SALKOWSKI (*Biochem. Zeitsch.*, 1920, **103**, 185—188).—The action of pyrrole on *p*-dimethylaminobenzaldehyde resembles that of indole, only it is less sensitive and is to a greater extent influenced by the addition of nitrite and fuming hydrochloric acid. The author points out the necessity of taking this fact into consideration when carrying out Ehrlich's reaction.

S. S. Z.

**Combination of Fractionation with Spectrophotometry in Proximate Organic Analysis.** W. E. MATHESON (*J. Amer. Chem. Soc.*, 1920, **42**, 1277—1279).—The spectrophotometric method of estimating dyes may be applied to colourless organic compounds by first converting these into coloured compounds, which are separated from the excess of reagents or other coloured substances present by extraction with suitable solvents. Procedures are described for the estimation of sulphanilic acid, acetone, and  $\beta$ -naphthol, depending on their condensation, respectively, with picryl chloride, 2:4-dinitrophenylhydrazine, and diazotised sulphanilic acid.

J. K.

**Justification of the Sublimate-Ammonia Process for the Estimation of Stercobilin.** R. GOFFRON (*Compt. rend. Soc. Biol.*, 1920, **83**, 344—346; from *Chem. Zentr.*, 1920, ii, 755).—A reply to Borriën's objections (this vol., ii, 520).

E. H. R.

**The Extraction of Stercobilin.** M. BRULÉ and H. GARBAR (*Compt. rend. Soc. Biol.*, 1920, **83**, 342—344; from *Chem. Zentr.*, 1920, ii, 754—755).—The extraction of stercobilin from excrement by solvents, such as amyl alcohol, chloroform, a mixture of chloroform and thymol, or 95% alcohol, is not complete. The extraction is better from acidified solutions, but under these conditions a change of the colouring matter appears to be brought about through oxidation.

E. H. R.

**Analysis of the Colouring Substances in Urine. I. The Division of Urine into Three Main Fractions as a Basis for the Analysis of its Colouring Substances.** M. WEISS (*Biochem. Zeitsch.*, 1920, **102**, 228—246).—The urine is divided into three fractions. Fraction I consists of the red colouring substances—the urobilin fraction. Fraction II contains the yellow colouring substances—the urochrome fraction. Fraction III is composed of the colourless proteic acids—the histidine fraction. Fraction I, which is obtained by precipitating the urine with neutral lead acetate, and does not contain the urochrome, is responsible for about three-quarters of the coloration of the urine. Fraction II is precipitated from the filtrate of fraction I with 10% alkali hydroxide. Besides urochrome, this fraction contains urochromogen, which differs from urochrome by the fact that it gives the permanganate and diazo-reactions, reduces silver salts, and darkens more intensely on keeping, when a melanin group is eliminated, which the author considers to be a phenol derivative. The presence of urochromogen can be detected better in fraction II than in the original urine. The colourless fraction contains proteic acids. A tryptophan derivative is also present in the urine, which cannot always be identified with the chronogen of urosoein.

S. S. Z.

**Chemistry of the Proteins.** E. HERZFIELD and R. KLINGER (*Biochem. Zeitsch.*, 1920, **102**, 89—98).—In order to obtain proteins free from adhering impurities, such as the products of protein degradation, fats, lipoids, etc., the clear extract from the tissues is precipitated with five to six volumes of 90% alcohol and heated on a boiling-water bath. It is then filtered or centrifuged, and the residue treated with boiling absolute alcohol, and again with boiling ether. The protein powder thus obtained is further extracted with boiling water to remove the albumoses, peptones, and salts. The authors also describe a method for the detection and estimation of the higher polypeptides in the protein solution. The protein and the higher polypeptides are precipitated with boiling 90% alcohol. The precipitated fraction is then extracted with boiling water, and the nitrogen is estimated in the aqueous extract. Using this method, it is found that all colloidal protein solutions contain appreciable quantities of albumoses. One hundred c.c. of human serum contain a quantity of albumoses and peptones equivalent to 0.4 gram of Witte's peptone. S. S. Z.

**Rapid Estimation of Albumin in the Urine.** **L. DUPUY** (*Presse medicale*, 1920, **28**, 104).—The turbidity of a standard solution of albumin is compared with that of the urine under examination after each has been treated with Eschlach's citric-pieric acid reagent.

CHEMICAL ABSTRACTS.

**The Separation of Serum Proteins.** **M. PIETTRE** and **A. VILA** (*Compt. rend.*, 1920, **170**, 1466—1468).—The serum is first neutralised by addition of *N*-hydrochloric acid. To it is added two and a-half times its volume of acetone. The precipitate is collected on a Bucher funnel, mixed with one volume of acetone, dried by suction, and washed with ether. The cake of proteins, without being brokeu up too much, is transferred to a dish, covered with water (70 c.c. for each 100 c.c. of serum originally taken), and left in contact with it for several hours. The water is then carefully decanted, and this process is repeated two or three times. Finally, the material is powdered and washed two or three times by centrifuging with water saturated with carbon dioxide. By this means, the insoluble proteins are obtained free from albumin. The washing waters are united, saturated with carbon dioxide, and filtered, and from the filtrate the albumin is precipitated by the addition of an equal volume of acetone.

In the aqueous-acetone liquors, the fats, lipoids, sugars, etc., can be estimated separately by the usual processes. **W. G.**

**New and Improved Method for the Recognition of Human Blood.** **ANGELO DE DOMINICIS** (*Boll. Chim. farm.*, 1920, **59**, 241—244).—A simple method for detecting human blood on a knife-blade or other non-absorbent surface consists in pouring on to the spot a very dense solution of celluloid in amyl acetate, allowing the solvent to evaporate, removing the dry pellicle by means of needles, and examining under the microscope the superficial layer of blood on the pellicle. If the latter cannot be removed from the blood-stained surface, it may be first thickened by a second application of the celluloid solution. **T. H. P.**

**“Thiocol.”** **C. A. GRAU** (*Bull. Sci. pharmacol.*, 1920, **27**, 17—22).—A diagram of the crystals formed by the reaction of thiocol with mercurous nitrate is given, together with the directions for making this microchemical test. As with guaiacol, so with thiocol, it is possible to test various plants for oxydases in the presence of hydrogen peroxide. The roots of artichoke, dahlia, chard, and lucerne are suitable materials responding positively to the test. Thiocol can also be used to demonstrate the presence of oxydase in the blood, and as a measure of renal insufficiency. Its use in the latter connexion depends on its detection in the urine by the rose colour developed when a few drops of the urine are placed on artichoke root, together with hydrogen peroxide. Its use is apparently incompatible with the presence of resorcinol,  $\alpha$ -naphthol, and sodium salicylate.

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